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Advanced Inorganic Chemistry

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الكـيمـياء غيرالعضويه المتقدمه

Advanced Inorganic Chemistry

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المحتويات

مقدمة عامة

نظراً لخطورة الملوثات العضوية على البيئة ، وحرصا علي سلامة صحة الأنسان ونوعية مياه الشرب فقد أهتمت المواصفة القياسية لمياه الشرب رقم 458 لسنة 2007 بالمواد الغير العضوية تشمل مواد غير عضوية لها تأثير على الإستساغة والإستخدامات المنزلية وتضم 12 مادة منها عناصر الحديد، المنجنيز، النحاس، الزنك ، الصوديوم، والألومنيوم، كما أشتملت على المواد الغير عضوية على المواد الكيميائية ذات التأثير على الصحة العامة والتى وهى عناصر الرصاص،الزئبق، الزرنيخ، السيانيد، الكروميوم، الانتيمون، النيكل، الموليبدينيوم، الباريوم، الفلوريدات، النتريت، الامونيا و النترات. لذا فإن الطرق التقليدية أصبحت غير كافية لتقييم نوعية المياه من حيث صلاحيتها للاستخدام الآدمي.

ومن ثم فإن الهدف الرئيس من هذه الحلقة الدراسية هو؛ تمكين كل دارس من الوقوف على اسس الطرق الحديثة في تحديد وتقدير الملوثات العضوية متضمنة تطبيق برنامج QA/QC . وللتاكد من جودة ونتائج التحاليل تم الأهتمام ببرنامج (Quality assurance QA and Quality control) ليقوى ويجسد فعالية بيانات التحليل، لإزالة أو تقليل الأخطاء التى ربما تتواجد فى العمليات المعملية، والتى تتسبب من الأشخاص، والأجهزة، والأدوات, وطرق أخذ العينات، وطريقة التحليل. وتقييم المعمل تمهيدا لتطبيق برنامج التأمين والتحكم فى الجودة.

وبمعرفة الدارس أسس تلك النظم ومن خلال عمله وتطوير الأداء- بدءا من جمع العينات ، والتأكد من دقة أداء وسائل التحليل واتباع الطرق القياسية فى التحليل مع تطبيق برامج QA/ QC والتى من أهدافها تقليل الأخطاء فى المعمل والتى تنعكس على دقة النتائج المتحصل عليها - سيكون هناك فى النهاية سجلات للنتائج وتحليلها يمكن الاعتماد عليها لتأكيد سلامة مياه الشرب.

وفى نهاية البرنامج نكون قد أعددنا كوادر من الكميائيين على دراية كافية بالأسس النظرية والعملية لكيفية القيام بالتحاليل الكميائية للملوثات الغيرعضوية وفق برنامج التحكم فى جودة النتائج. وقادرين على نقل ما تلقوه خلال الدورة الى مجموعة أخرى من العاملين وبالتالى تتسع الخبرة النظرية والعملية ويتم تحديث خبراتهم بكل ما يخدم العاملين فى هذا المجال والذى بدوره ينعكس على نوعية المنتج من مياه الشرب.

ويشتمل البرنامج علي ستة فصول اساسية متضمنة شرح تفصيلي ومبسط

الفصل الاول: الملوثات الغيرعضوية

ويحتوي علي أنواع الملوثات الغيرعضوية وتقسيمها ومصادر تلوث المياة بتلك العناصر ومدى تأثيرها وخطورتها على صحة الإنسان.

الفصل الثاني: تقدير المعادن الثقيلة فى عينات المياه

وبشتمل أنواع طرق التحليل المختلفة وكيفية أخذ وحفظ العينات كما يتضمن مواصفات الأوعية المستخدمة فى الحفظ والطريقة المثلى لغسيل الأدوات.

الفصل الثالث :التحليل الكيميائي للمعادن Analytical Procedures for Metals

ويشتمل علي المعاملة الأولية للعينات وطرق الهضم المختلفة.

الفصل الرابع: أجهزة القياس المختلفة Ion coupled plasma (ICP)

ويتضمن مقدمة عن جهاز الامتصاص الذرى وكذلك جهاز اسس استخدام الجهازان وكذلك الأجزاء الرئيسية للجهازن وطريقة تحديد وتعين الملوثات، و الظروف المختلفة التي تؤثرعلي عمليات التحليل.

الفصل الخامس:التحقق من صحة النتائج :Quality Control

يتضمن هذا الفصل العناصر الأساسية لبرنامج التحقق من صحة النتائج ويحتوي علي تعريف الدراس بالعناصر الأساسية لبرنامج التحكم في جودة نتائج تحليل الملوثات العضوية، وكيفية القيام بالعمليات الحسابية لقياس دقة وحساسية وكفاءة الطريقة المستخدمة

الفصل السادس: تثبيت طريقة التحليل Method Validation

ويتضمن كيفية إختيار طرق التحليل للتثبيت كما يتضمن عناصر التثبيت وكيفية تحليل نتائج القياس

الفصل الأول

الملوثات الغيرعضويه

الفصل الأول

الملوثات غير العضوية

Inorganic Micropollutants

المقدمة

تمثل المياه العذبة إحدي ضرورات الحياة غير أنها بالنسبة للعديد من الأماكن نادرة وصعبة المنال. لذا فإن الحصول عليها سليمة نقية مطابقة للموصفات الصحية تعتبر الشغل الشاغل للمجتمع الدولي . ونتيجة للثورة الصناعية والازدياد في استخدام المبيدات والأسمدة العضوية والمواد البتروكيميائية ، أصبحت مياه الشرب عرضه للتلوث بالمواد العضوية والمعادن الثقيلة . بالإضافة إلى أن استخدام الكلور في عملية تنقية مياه الشرب ينتج عنه تكون مواد عضوية هالوجنية ذات تأثير ضار على صحة الإنسان ، مثل مشتقات الميثان وحمض الخليك الهالوجينية (Trihalomethanes and Haloacitic acids) . لذا فإن الطرق التقليدية لتحليل المياه بالرغم من أهميتها أصبحت غير كافية لتقيم نوعية المياه من حيث صلاحيتها للاستخدام الأدمي ، ومن هذا المنطلق وجب دراسة الطرق الحديثة لقياس العناصر المعدنية heavy metals analysis) و تقسم العناصر المعدنية (Heavy Metals) إلى :

- عناصر معدنية كبرى (Macro : Major Elements): وتمثل 35 % من وزن الجسم مثل الكالسيوم (1.2 – 2 %) والفسفور (0.07) والصوديوم والبوتاسيوم والكلور والكبريت والماغنسيوم.

- عناصر معدنية صغرى ضرورية للجسم (Micro : Essential elements):

وقد تسمى بالعناصر الدقيقة كالحديد والزنك والنحاس ولامنجنيز والكوبلت واليود والمولبيدنيم.

- العناصر المحتمل أنها ضرورية للجسم **(Possibly Essential Elements):** كالرصاص والكادميوم والزرنيخ والسلينيوم والفلور والفان ديوم والكروم والقصدير والنيكل والسيليكون والبرورون والباريوم.

- كما توجد عناصر غير ضرورية للجسم ملوثة (Non Essential Elements:Contaminant) مثل الألومنيوم والأنتيمو ن والبزموث والجرمانيوم والذهب والفضة والربيديم و هذا يؤدى الى إصابة الانسان بالعديد من الأمراض نتيجة تلوث مياه الشرب.

1 - تلوث المياه بالرصاص (water Lead Pollution) :

تتلوث المياه بعنصر الرصاص نتيجة ملامسة الهواء الملوث به للمسطحات المائية أو الهواء الملوث بعادم السيارات أو مداخن مصانع الكبريت والطلاء والورق والقصدير والصفيح كما يمكن وأن تتلوث المياه نتيجة طلاء الخزانات وأنابيب المياه والجدران الداخلية أو يستخدم فى اللحام والذى يتحول لكربونات رصاص لا تنحل فى الماء فيعق تسرب الرصاص من جديد للماء وتزداد نسبة الرصاص فى الليل والصباح الباكر لركوده المياه به. أو قد يكون مصدر التلوث هو سحب ملوثة به وممطرة وقد يكون مصدر التلوث هو صرف مياه مخلفات المصانع بالأنهار والبحار القريبةمن هذه المصانع.

وتبلغ نسبة الرصاص بالمياه 10^{-1} ميكروجرام/لتر (010^{-1} جزء فى البليون : ppb). ولوحظت زيادة فى تركيز الرصاص بشك عالى مخيف فى الآونة الأخيرة فى مياه المحيطات فتضاعفت خمس مرات خاصة فى شمال المحيط الأطلنطى وكذلك بلغ عدة أجزاء فلا المليون على المياه الإقليمية لشواطئ لبنان (أى على بعد يبلغ 220 متر من الشواطئ) فى حين بلغت مستوى هائل ومخيف للغاية (150 – 480 جزء فى المليون) بأنسجةالكائنات البحرية فى خليج تسالونيك خاصة بالقرب من معمل إنتاج مركب تترا إيثيل الرصاص.

وتراكم جزيئات الرصاص بأنسجة الكائنات الحية كالطحالب والقشريات ومن كلاهما ينتقل عبر السلاسل الغذائية الحيوانية ويصل فى النهاية للانسان.

ارتفاع نسبة الرصاص عن 0.1 ملجم/ لتر (0.1 جزء فى المليون) بمياه الشرب يؤدى لظهور أعراض التسمم بالرصاص فى صورة خطوط زرقاء مسودة باللثة وتكسير كرات الدم الحمراء وإمساك انخفاض نسبة الهيموجلبين مع ألم بالصرة أو تحتها وبزيادة شدة الأعراض تؤدى لإضطرابات عصبية تصل للشلل الطرفى والصرع والتشنجات ثم غيبوبة (comma). كما أنه يعوق إفراز حمض اليوريك مما يؤدى لظهور أعراض مرض النقرس.

وتحتوى المياه السطحية على مستوى من الرصاص يبلغ 10 ميكروجرام / لتر 10 جزء فى البليون : 0.010 جزء فى المليون / لتر) ويجب عدم استخدام مياه الشرب التى تصل فيها تركيز الرصاص إلى 50 ميكروجرام/لتر (0.050 جزء فى المليون) حيث يترسب فى

الأنسجة العظمية والكبد والكليتين فى فى صورة ثالث فوسفات الرصاص يتراكم بالعظام مع فترات التعرض الطويلة ويحل محل الكالسيوم كما يتراكم بأنسجة المخ فيتلفها مما يؤدى للصرع بوصول تركيزه إلى 100 ميكروجرام/ لتر (0.1 جزء فى المليون) يصبح الماء السام). ولذا يجب استخدام مياه الصنبور العادى بالمنزل ترك المياه تتدفق بدون استخدام لعدة ثوانى دون استخدامها حيث يتسنى التخلص من نسبة عالية من الرصاص بها. ويوجد الرصاص بكميات ضئيلة بالجسم حيث يدخل عن طريق الفم عند الشرب للمياه الملوثة به حيث تفرز نسبة منه بالبراز وأخرى بالبول عن طريق الكليتين ونسبة ثالثة تمتص وتصل حتى 20% وتتحرك لكبد الذى بدورة يحركها مع العصارة الصفراء للأمعاء (فى حين يدخل الرصاص مع الهواء الملوث المستنشق خلال الشعب الهوائية للدم ولا يمر عن طريق الكبد) ، ونظراً لتشابه عمليتى تمثيل الرصاص والكالسيوم فى الجسم فأن العوامل المحفزة لتخزين الكالسيوم بالجسم تكون هى نفسها العوامل المحفزة لتخزين الرصاص.

ويؤدى التسمم المزمن بعنصر الرصاص إلى تبلد فكرى وتخلف عقلى وعدم المقدرة على التركيز مع ضعف فى الذاكرة وصمم وفقدان النطق أو العمى ثم الشلل لليد اليمنى ثم اليسرى وأخيراً شلل المخ وفشل كلوى.

أما بالنسبة للأطفال فزيادة نسبة الرصاص بأجسادمهم تؤدى لانخفاض مستوى الذكاء بوضوح (وذلك لزيادة نشاطهم مع قلة محتوى أجسامهم النسبى من الدم).

ويلاحظ أن وجود الرصاص بدم الأم الحامل (8 ميكروجرام/100 ملل دم) يؤدى لولادة أطفال يحتوى دمهم على نسبة كبيرة من الرصاص وقد يصل إلى 25 ميكروجرام/100 ملل دم كما يؤدى الرصاص بدم الأم إلى ولادة أطفال ذات أوزان أقل من المتوسط بحوالى 200 جم وضعاف لإستجابة المؤثرات البصرية والسمعية لحوث إعاقة فى نمو خلايا المخ.

2 - تلوث المياه بالزئبق (water Mercury Pollution) :

تعد ملوثات الزئبق العضوية أشد خطراً وسمية على الصحة العامة عن مركبات الزئبق الغير عضوية والتى يمكن لجسم الانسان إفرازها بالبول (مثل الزئبق – فينيل خلات الزئبق – داى ميثيل الزئبق).

ويكمن سبب خطورتها وسميتها العالية فى درجة ثباتها العالية (High stability) وتراكمها الحيوى (Bio accumulation) داخل أنسجة الجسم خاصة بأنسجة المخ فتسبب شلل وتشوهات (Teratogenic) وضعف بالبصر والسمع علاوة على كونها مواد مطفرة

(Mutagenic) فكلما زادت درجة صعوبة تحللها كلما زادت درجة خطورتها كما تتراكم بأنسجة السمك الموجودة فى مياه ملوثة يصل تركيزها بها 0.1 ميكروجرام/لتر (0.0001 جزء فى المليون) وعند بلوغ مستوى تركيزه فى مياه الشرب سامة حيث أن أقصى حد مسموح بتواجد فى الماء هو 0.001 ملجم/ لتر وتزداد خطورة الزئبق اللاعضوى بتحوله لمركبات زئبق عضوية سامة كمثيل الزئبق للكائنات الحية الدقيقة حيث أن المركبات الزئبقية العضوية أشد سمية وخطراً على الإنسان فهى تمتص وتتراكم فى حين أن المركبات الزئبق العضوية يتم إخراجها عن طريق البول.

كذلك أظهرت التقارير عن تحليل عينات بروتين سمكة تم صيدها من بحيرة سانت كلير بكندا احتواءها على الزئبق فى صورة ثنائى فينيل الزئبق يرتبط بالبروتين عن طريق ذرة الكبريت كذلك كان الحال فى بحيرة ليمان بسويسرا خاصة ف فى حالة العوالق (الهائمات) النباتية والجسيمات والتى أعزيت لصرف مياه المصانع فى مياه نهر الرون الذى تصل مياهه للبحيرة.

ويلاحظ أن تركيزه يزداد تركزاً بارتقاء كائنات السلاسل الغذائية فهو بالإنسان > الطيور > الأسماك > القشريات > النباتات > الهائمات ويعزى ذلك لزيادة معدل تراكمه الحيوى على هذا النحو وهو ما يسمى بالتضخم الحيوى (Bio magnification) كما ظهر أثره الواضح فى التراكم الحيوى والتضخم بوضوح فى مرض الميناماتا والذى ترجع تسميته إلى خليج ميناماتا فى اليابان حيث أدى صرف أحدى مصانع البلاستيك لمخلفاته فى مياه الخليج وكانت محتوية على 501 جزء فى المليون زئبق مما أدى لتسمم الأسماك والصيادين وظهرت الأعراض فى صورة لعثمة فى النطق وزغلله وشلل بالأطراف لتدمير الخلايا العصبية فى المخيخ والمخ الأوسط كما أدى لحدوث بعض حالات تغير جينية.

كما أدت إلقاء فضلات مصانع الزئبق لزيادة نسبة وفيات سكان نهر دامسى فى واشنطن أونهر هومسون فى نيويورك وبحيرة توركش بولاية ميتشجان ولهذا قامت سلطات هذه الولايات الثلاثة بحظر السباحة أو تناول المياه أو الأسماك من هذه المصادر الثلاثة.

ولقد بلغت نسبة الزئبق بالسواحل العربية على البحر الأبيض المتوسط 1 ملليجرام / كم سمك وهو ما يشير بأنه عند استهلاك 2 كم سمك أسيوى يؤدى بدور لامتصاص ما يوازى 2ملليجرام يثبت منها 80 ميكروجرام بالجسم / أسبوع وعليه تظهر أعراضه (تأثيراته) الأولى بعد 7 سنوات وتحدث الوفاة بعد 20 عام ومما يجدر بالذكر فى هذا الصدد وهو ما أثار الدهشة تواجد تركيزات ملحوظة من الزئبق فى الحيوانات القطبية كالدب القطبى

والطيور كالبنجوين رغم رغم بعهدها عن مصادر التلوث به وقد أعزى ذلك إلى حدوث تلوث بإحدى مراحل السلسلة الغذائية حيث انتقلت متبقيات الزئبق لها خاصة الأسماك.

وتقوم الكائنات الحية الدقيقة الغير هوائية مثل بكتيريا Closrtidum Cocheaealcor والتى يكثر وجودها فى الترسبات المائية بتحويلها لمثيل الزئبق أو داى ميثيل الزئبق وهو أشد سمية.

3 - تلوث المياه بالكادميوم (Water Cadmium Pollution) :

يتم تلوث المياه بعنصر الكادميوم نتيجة إلقاء مخلفات المصانع والتى تصل إلى 1000 طن سنوياً من معدن الكادميوم فى المسطحات المائية خاصة مخلفات مصانع المواسير والطلاء أو لمرور مياه بمواسير بلاستيك يدخل فى تركيبها. والكادميوم ملوث خطر جداً لتراكمه بأجسام الكائنات الحية النباتية والحيوانية خاصة المائية منها كالسمك والقشريات وأخيراً يصل الانسان بقمة السلسلة الغذائية (Food chain).

ويجب ألا يزيد مستوى تواجده بالمياه عن 120 ميكروجرام / لتر (12 % جزء فى المليون) وزيادة مستواه عن ذلك تجعل المياه غير صالحة للاستخدام الآدمى وهنا يجب الأخذ فى الاعتبار أن مواسير المياه البلاستيكية الصنع تؤدى إلى تسرب الكادميوم من مادتها للمياه المارة فيها وعند بلوغ مستواه بالمياه إلى 200 ميكروجرام / لتر (0.2 جزء فى المليون) وتصبح المياه مميتة ، حيث يؤدى الكادميوم إلى اضطراب فى النمو العام مع تغيير فى تركيب الدم وفقر الدم (أنيميا) وظهور مرض (أيتاى – أيتاى) كذلك حدث تسرب للكادميوم من نفايات إحدى المصانع المطلة على نهر بالبرازيل للحالات تسمم فى صورة اضطرابات عصبية وارتفاع فى ضغط الدم حيث بلغت نسبته بأجسام أسماك مياه النهر إلى 21 مللجرام / كجم سمك.

4- تلوث المياه بعنصر الزرنيخ (Water arsinous pollution) :

يحدث تلوث المياه بعنصر الزرنيخ من عدة مصادر أكثرها التعرض لبقايا السموم الزرنيخية المستخدمة فى مكافحة الآفات الحشرية والحيوانية والحشائش سواء لأنجرافه فى الهواء (Drift) أثناء الرش أو أثناء التعفير وسقوطها على الأسطح المائية المحيطة أو المترسبة منها على الأسطح المعاملة والتربة والحادث لها عملية سريان (Dripping : Run off) أو الغسيل (Washing) ثم تتخلل حبيبات التربة وتتشرب (Leashing) حتى تصل إلى المياه الجوفية وكذلك مياه صرف المصانع والقائمة بطحن وتجهيز مستحضراته.

ويلاحظ أن مركبات الزرنيخ الثلاثية أشد فى درجة سميتها عن الخماسية (Penta vallant) لارتفاع معدل ذوبان الأولى كثيراً فى الماء (حيث لمعدل الذوبان وكذلك درجة نعومة المادة أثرهما الفعال فى ارتفاع السمية فكلما زادت درجة النعومة كلما زاد معدل التخلل والامتصاص ، كذلك فكلما زادت نسبة الذوبان زادت نسبة انفراد الزرنيخ الذائب فى الماء) (حيث تؤدى ارتفاع درجة الحرارة أو الرطوبة النسبية أو الندى أو زيادة نسبة ثانى أكسيد الكربون بالجو كذلك المناطق الساحلية حيث زيادة مستوى كلوريد الصوديوم بالجو إلى زيادة انفراد الزرنيخ الذائب) والتالى تزداد درجة السمية والضرر الجانبى على النباتات والحيوانات وبامتصاصها بالجسم خلال الجلد أو بوصولها للقناة الهضمية عن طريق شرب مياه ملوثة بها أو أطعمة تحتوى على مخلفاتها تبدأ أعراض التسمم المعدى فى صورة آلام شديدة بالمعدة ثم اسهال وتبول مدمم وشحوب وبرودة بالجسم مع العطش ونقص التنفس ثم يدخل فى الغيبوبة فالوفاة ، حيث تبلغ الجرعة القاتلة 5 – 100 مللجرام / كجم من وزن الجسم تبعاً لنوع الكائن المعامل ونوع المركب الزرنيخى.

وبوصولها للجسم ترتبط بذرات كبرت المستقبلات الحيوية (Bio receports) خاصة الإنزيمات المحتوية على مجاميع سلفهيدريل (-SH) فتثبطها مثل إنزيم لاكتيك ديهيدروجينيز وألفا جلسرو فوسفات ديهيدروجينيز والسيتوكروم أكسيديز فهى تستهدف روابط الكبريت وتكوين مركبات كبريتية فتختفى مجاميع السلفهيدريل الحرة والتى تقوم بدور كبير فى المحافظة على على الشكل المميز للبروتين لذا فالحقن بالجلوتاثيون أو البال (PAL) يمنع استمرار التسمم لتنافس مجاميع السلفهيدريل على جزئيات الزرنيخ وترتبط به وتبعده عن الأنسجة بما يؤدى لعمليات ترسب : تجلط (Coagulation) خاصة عند ارتفاع تركيزه فجزيئات المركبات الزرنيخية تستهدف فى المقام الأول روابط الكبريت والتى لها دورها الهام فى حفظ الشكل البنائى المميز (Configuration) لجزئيى البروتين.

كما ترتبط مع المرافق الأنزيمى (أ) الأنزيمات التى تقوم بنزع الهيدروجين من المركبات الحيوية أو ترتبط بالمواد المؤكسدة فتمنع عملية الفسفرة التأكسيدية لجزيئات الأدينوسين داى فوسفات (ADP) وتكوين الناتج المفسفر (ATP).

ويلاحظ إمكانية تخلص الجسم من التركيزات المنخفضة بواسطة الكلية وإخراجها عن طريق المسار البولى وفى بعض الأحيان يفرز فى البراز حيث ظهر فى الأبقار لمدة تصل إلى 14 يوم بينما وصلت فى البراز حتى 70 يوم وهنا يجب الأخذ فى الاعتبار فى هذا الصدد بأن التركيزات الضعيفة منه تعد منشطة للجسم وفاتحة للسهية (أكلة الزرنيخ) أما فى تايوان فينتشر مرض القدم السوداء (Black foot) لارتفاع مستوى الزرنيخ فى مياه الشرب الجوفية كذلك وجدت تركيزات عالية منه فى مياه شرب بقرية توربوان بالمكسيك (4-6 جزء فى المليون).

أما عند التعرض لجرعات عالية عن الحد الذى يمكن عنده أن يتخلص الجسم منها فإن الزائد منها يتجمع بالدرجة الأولى بالكبد فيسبب تدهن الكبد (Fatty Liver) ثم الكلية ثم بعض الأنسجة الأخرى كالعظام والجلد والأظافر والشعر.

أما بالنسبة لتأثيرات مركبات الزرنيخ السامة على النباتات التى يتخللها سواء عن طريق المواضع الرقيقة فى كيوتيل الأوراق بالمجموع الخضرى حيث يبقى بها ولا يتحرك. ويلاحظ أن درجة التخلل تزداد بارتفاع الرطوبة أو عن طريق الجذور فترتفع فيها لأعلى بالمجموع الخضرى وهنا يؤثر كسم بروتوبلازمى (Protoplasmic poisons) فتسود الأوراق وتموت (حروق موضعية). وتحدث عقب عملية إمتصاصه خلال المجموع الخضرى زيادة سرعة التنفس وهنا تتحول الأوراق للون الأصفر ثم تسقط.

4- تلوث المياه بالنحاس Water Copper pollution:

يدخل النحاس الجسم عن طريق المياه والأغذية الملوثة أو الهواء الملوث ثم يمتص بالأمعاء معتمداً على البروتين المرتبط (Metallothionine) بآلية غير واضحة للآن وله فى ذلك علاقة بالزنك والكادميوم وسرعان ما يرتبط بألفا-جلوبين : سيرولوبلازمين (Ceroloplasmine) ويخزن بالكبد كبروتين يسمى (Hepatocupreina) حيث يطلق على هذا البروتين بروتين كرات الدم الحمراء (Cerebrocuprin) خلايا الأعصاب اسم مشترك هو (Cytocuprin).

يطرح النحاس خارج الجسم عن طريق البراز مع إفرازات الصفراء أو يخرج فى البول (4%). ويدخل فى عمل أنزيم السيتوكروم أكسيديز (Cytochrome Oxidase)

والأسكوربيك أكسيديز (Scorpic Oxidase) والتايروسينتيز (Tayro synthetase) واليويكيز (Uricase) وضورى لتمثيل الطاقة وتكوين الهيموجلوبين. كذلك فوجوده يحسن من امتصاص الحديد من خلايا جدر الأمعاء وتحركه بين الكبد للبلازما لبناء الهيموجلوبين كما يدخل فى تكوين العظام والميلين بالمخ ولذا فنقصه (Hypocupremia) تؤدى لمرض الكلى والتخلج (Neonatal Ataxia) والسقوط (Falling disease) لضمور وتليف عضلة القلب ونقص الإخصاب وموت الجنين وضعف التنفس وتشوه الأجنة أما زيادة مستواه بالدم والأنسجة خاصة أنسجة الكبد فيؤدى لمرض ويلسون (Wilson) لحدوث تغيرات بنسيج المخ والكبد فيتراكم بالكبد وقرنية العين والكلى والمخ ويعالج بالمواد المستحلبة (Penicillamine) والزنك الذى يزيد إفرازه خارج الجسم والتسمم الحاد بالنحاس نادر ما يحدث يتطلب ذلك جرعة تبلغ 20 ملجم / كجم.

وتؤدى زيادة مستوى المولبدينم (Molybdenum) بالجسم لزيادة فقد النحاس بالبول إلا أنه يقى الأسنان من التسوس ربما لأثره فى الاحتفاظ بالفلور بالجسم ويلاحظ أيضا ارتباط الأعراض معاً فزيادة بالجسم تؤدى للتسمم وظهور مرض (Peat scours) والمعالج بإعطاء مركبات محتوية على النحاس لتضاد فعلها أما نقص المول بيدينم فيؤدى لإسهال ونقص النمو وفقد الدم وتأخر نضج كرات الدم.

5- تلوث المياه بعنصر الحديد water Iron Pollution

حيث يكون صورته بالماء على هيئة ملح ذائب هو بيكربونات الحديد التى بتعرضه للهواء الجوى يتحول للون الأحمر فالبنى. وتلوث المياه بالحديد لا يغير من طعمها ولكن زيادة مستواه عن 0.3 ملجم / لتر يؤدى لعسر فى الهضم وإمساك. وتحتوى بعض مصادر المياه الجوفية على تركيزات تصل 5-7 ملجم / لتر.

الفصل الثـــانى

تقدير المعادن الثقيلة فى عينات المياه

الفصل الثانى

تقدير المعادن الثقيلة فى عينات المياه

A. أنواع طرق التحليل المستخدمة:

- هناك طرق عديدة تستخدم لتقدير المعادن فى عينات المياة.
- يتم أختيار الطريقة تبعا للحساسية والدقة المطلوبة فهناك طرق التحليل اللونية وهناك طرق بإستخدام الأجهزة.

- Flame atomic absorption methods concentration is (0.1 to 10 mg/L) Electrothermal methods
- Inductively coupled plasma emission techniques (حد التقدير أقل من 0.01 ميكروجرام لكل لتر)
- Flame Photometry يعطى حساسية افضل لقياس التركيزات العالية لعناصر المجموعة الأولى والثانية.
- Anodic stripping
- Colorimetric methods

تعريف المصطلحات: Definition of terms

العناصر الذائبة: Dissolved metals

العناصر الذائبة فى العينة الغير معاملة بالحامض والتى يمكن ان تمر خلال غساء ترشيح 45ميكروميتر

Suspended metals: العناصرالمعلقة

يقصد بها العناصر المعلقة فى العينة الغير معاملة بالحامض ولا تمر خلال غساءالترشيح بينما تحجز على الغشاء(45ميكروميتر).

Total metals: مجموع المعادن

يقصد بها تركيز المعادن الموجودة فى العينة بعد عملية الهضم أو مجموع تركيزات المعادن الذائبة والمعلقة ويتم تقديرها

Acid- extractable metals: العناصر التى يمكن استخلاصها بالحامض

تركيز المعادن فى العينة بعد معالجتها بمحلول الحمض الساخن.

B) Sampling and Sample preservation: عملية أخذ وحفظ العينات

- تتوقف العملية على نوعية الجزء المراد تحليلة والذى بدورة يحدد إذا كان سوف يتم معالجة العينات بالحامض وترشح أم تهضم.

Sample containers: الاوعية المستخدمه

- تفضل الاوعية المصنوعة من الكوارتز أو مادة TEF وكذلك يمكن أستخدام الاوعية البلاستيكية المصنوعة من polypropylene or linear polyethyleneمادة البولى بروبيلين أو البولى إثيلين بأغطية مصنوعة من مادة البولى إثيلين (polyethylene cap)
- كما يمكن إستخدام الاوعية الزجاجية المصنوعة من البوروسليكات borosilicate glass containers
- يحذر من إستخدام soft glass لإحتوائة على شوائب معدنية بتركيزات (ug/L)
- يراعى شطف الاوعية المستخدمة وكذلك ورق الترشيح بالحامض.

Sample preservation: عملية حفظ العينات

- يتم حفظ العينات بعد أخذها مباشرة وذلك بإضافة كمية من حمض النيتريك المركز الى أن يصبح الوسط الحامضى أقل من 2.
- لتقدير العناصر الذائبة : يتم ترشيح العينة قبل عملية الحفظ وعادة يتم إضافة (1.5 ml of HNO3/L sample) or (3 ml 1 + HNO3 /L sample) وهذة الكمية تكون كافية لحفظ العينة لفترة قصيرة.
- يجب إستخدام حامض مركز ذو درجة نقاوة عالية .
- يتم حفظ العينات عند درجة حرارة 4 درجة مئوية بالثلاجة لمنع التغير فى الحجم
- يمكن الإحتفاظ بالعينة لمدة 6 أشهر For mg/kg levels- ماعدا فى حالة الزئبق فيمكن حفظها لمدة 5 أسابيع فيجب تحليل العينة فى الحال (For ug/kg levels).
- **كيفية حفظ العينة لتقدير عنصر الزئبق:**
- تحفظ العينة بإضافة (2 ml of 20% $K_2Cr_2O_7$ / L of sample) (محضرة فى 1+1 حمض النيتريك):

إحتياطات عامة :

مصادر تلوث العينات :

- الأوعية المستخدمة لحفظ العينات – الأغشية المستخدمة فى الترشيح _ أغطية الأنابيب البلاستيكية ربما تكون مصدر للتلوث ببعض المعادن مثال (Cd, Zn)

2- **كيفية اتخلص من الملوثات:** وذلك من خلال إستخدام أدوات نظيفة:

- **الطريقة المتبعة لغسيل الأدوات:**
  - يتم غسيل الأدوات بمحلول غسيل خالى من المعادن
  - ثم يتم الشطف بالماء وينقع فى الحامض
  - ثم يتم الشطف بالماء المقطر

- **طريقة غسيل الأدوات الزجاجية المصنوعة من الكوراتز او TEF glass materials**

- Use (1+ 1 HNO_3) , (1+1 HCl) or aqua regia (3 parts conc. HCl + 3 conc. HNO_3)

- **طريقة غسيل الأدوات البلاستيكية:**

- Use 1+1 HNO_3 or 1+1 HCl
- يتم نقع الأدوات لمدة 24 ساعة عند 70 درجة مئوية.

ملحوظة:

- للتخلص من الرواسب العضوية يتم نقع الأدوات فى حمض الكروميك مع مراعاة عدم إستخدام حمض الكروميك مع الأدوات البلاستيكية.
- يتم إستخدام ماء منزوعة الأيونات .

الفصل الثـــالث

التحليل الكيميائي للمعادن

الفصل الثالث

التحليل الكيميائي للمعادن

Analytical Procedures for metals analysis

ا) المعاملة الاولية للعينات Preliminary treatment of samples

- يتم معاملة العينات التى تحتوى على جزيئات او مواد عضوية الى معاملة اولية قبل اجراء عملية التحليل الأسبكتروسكوبى spectroscopic analysis لتحليل مجموع المعادن (تشمل المعادن العضوية والمعادن الغير عضوية الذائبة والغير ذائبة).
- يتم قياس العينات عديمة اللون والواضحة (مياة الشرب) مباشرة بدون هضم العينة لتقدير مجموع المعادن بدون هضم العينة.
- عند تجميع العينات يتم اضافة (1.5 ml HNO_3 / 1L) حتى يصبح الوسط الحامضى اقل من 2 وحينئذ يتم تحليل العينة مباشرة.

▪ **لتقدير المعادن الذائبة (dissolved metals):**

يتم ترشيح العينة ثم يضاف الحمض الى الراشح ويتم حفظة بالثلاجة الى ان يتم تحليلة.

▪ **لتقدير المعادن الغير ذائبة (suspended metals) :**

يتم ترشيح العينة ثم يتم هضم ورقة الترشيح والمادة العالقة بها.

▪ **لتقدير المعادن التى يمكن استخلاصها بالحمض (acid- extractable metals):**

يتم استخلاص المعادن يتم تحليل الراشح

▪ **معا ملة المعادن التى يمكن استخلاصها بالحامض (Treatment for acid – extractable metals)**

يتم اضافة 5 مللى من حامض النيتريك لكل لتر من العينة عند جمع العينة.

- **تحضير العينة :**

  - ينقل 100 ميللى من العينة الى كأس أو دورق ثم يضاف 5 ميللى 1+ 1 من حمض الهيدروكلوريك المركز عالى النقاوة.
  - يتم التسخين لمدة 15 دقيقة فى حمام مائى.
  - يرشح المحلول بواسطة عشاء ترشيح (45 µm).
  - يتم نقل الراشح الى دورق معيارى اخر ثم يكمل الحجم الى 100 ميللى بالمء الخالى من المعادن.
  - ملحوظة: اذا كان حجم العينة أكبر من 100 ميللى فانة يتم تقدير الحجم الى اقرب 0.1 ml / weight ثم يتم تحليل العينة ويتم تصحيح قياس التركيز النهائى بالضرب فى معامل التخفيف (الحجم النهائى \100).

ب) هضم المعادن Digestion of metals

- يجب اختيار طريقة هضم مناسبة للتقليل من التداخل (interferences) الناتج من وجود المواد العضوية ولتحويل المعادن المرتبطة بالجزيئات لتكوين شكلا من اشكال المعدن (عادة المعدن الحر free metal) التى يمكن قياسها بجهاز الامتصاص الذرى او جهاز ICP.

1- إختيار الأحماض Selection of acids :

- يستخدم حامض النيتريك فى هضم معظم العينات وذلك لكون النيترات matrix ملائم للحقن على أجهزة الامتصاص الذرى و اجهزة ICP – MS.
- تحتاج بعض العينات الى إضافة احماض أخرى لإتمام عملية الهضم مثل احماض (H_2SO_4- HCl- HF- $HClO_4$) ولكن تلك الأحماض ربما تحدث تداخلات interferences عند تحليل بعض العناصر حيث انها تعد (poorer matrix) للتحليل على أجهزة الامتصاص الذرى و اجهزة ICP – MS.
- يستخدم حمض النيتريك عادة بمفردة فى عملية الهضم لهضم العينات سهلة الأكسدة او يتم إضافة حمض الكبريتيك او حمض الهيدروكلوريك الى حمض النيتريك عند هضم المواد العضوية القابلة للأكسدة readily oxidizable organic matter و بينما يتم اضافة حامض البيركلوريك أو الهيدروفلوريك الى حمض النيتريك عند هضم المواد العضوية صعبة الأكسدة او المعادن التى تحتوى على سليكات.

2- طرق الهضم Digestion procedures

- الهضم بإستخدام المسطح الساخن Hot plate techniques
- الهضم بإستخدام الميكروويف (Closed vessel procedure)
- اذا كان الحجم الموصى بأخذة من العينة أكبر من سعة الدورق المستخدم فى هضم العينة فيجب تبخير العيتة .
- إذا تم تركيز العينة اثناء عملية الهضم (أكبر من 100 مللى) فإنة يتم تقدير معدل الإسترجاع لكل matix يتم هضمة وذلك للتحقق من صحة الطريقة.
  - ملحوظة : كلما إزداد حجم العينة كلما إزداد ت كمية الحمض المستخدم مما يؤدى الى زيادة الشوائب impurities

Estimated metal concentration تركيز العنصر (mg/L)	Sample volume (ml) *حجم العينة
< 0.1	1000
0.1- 10	100
10- 1000	10

*For flame atomic absorption spectrometry

metal concentration (تركيز العنصر) =A* B/C

A= concentration of metal in digested soln (mg/kg) تركيز العينة فى المحلول المهضوم

B = final volume of digested solution, ml, and الحجم النهائى للمحلول المهضوم

C= sample size, ml حجم العينة

Standard Method 3030 E

1. (الهضم بإستخدام حامض النيتريك Nitric acid digestion)

Digestion for flame atomic absorption and high – level concentrations

التقدير بإستخدام جهاز الأمتصاص الذرى المزود بوحدة اللهب لتقدير التركيزات العالية

- **الأجهزة المستخدمة: Apparatus**
  - مسطح ساخن Hot plate
  - دورق مخروطى سعة 125 ميللى أو كاس جريفين سعة 150 ميللى
  - 150 ml conical flasks (erelenmeyer) 125 ml or Griffin beakers

يتم غسلها بالحامض ثم تشطف بالماء المنزوعة الأيونات

  - دورق معيارى سعة 100 ميللى.
  - زجاجات ساعة watch glasses, ribbed and unribbed

الكواشف Reagent :

- حامض النيتريك المركز ذو درجة نقاوة عالية (analytical grade or trace metals grade)

الطريقة:

- ينقل 100 ميللى من العينة (المعاملة بالحامض) الى قارورة او كأس ثم يضاف 5 ميللى من حامض النيتريك المركز.
- يتم وضع رقائق الغليان او خرز زجاجى ليساعد على الغليان وتضبط درجة الحرارة.
- يتم تبخير العينة الى اقل حجم ممكن (الى حوالى من 10 الى 20 ميللى) .

- يمكن إضافة كمية أخرى من حامض النيتريك المركز لاتمام هضم العينة الى ان يصبح محلول العينة فاتح اللون وشفاف.
- يتم شطف جدران الدورق وزجاجة الساعة بالماء المقطر وترشح العينة إذا لزم ذلك.
- ينقل الراشح الى دورق معيارى سعة 100 ميللى على مرتين ب 5 ميللى من الماء المقطر.
- يترك المحلول ليبرد ثم يكمل الحجم الى العلامة ويمزج جيدا.

2. Determination for trace – level (<0.1 mg/l) concentrations for ICP and ICP-MS

- **الأجهزة المستخدمة : Apparatus**

- **سخان كهربى مزود بوحدة تحكم فى درجة الحرارة Block heater, dry, with temperature control**
- **انابيب من البولى بروبيلين مدرجة (تغسل بالحامض ثم تشطف بالماء المقطر)**

Polypropylene tubes, graduated, rounded, round- bottom tubes with caps 17x100 mm.

- Pipetters, assorted sizes or adjustable
- Pipette tips
- Centrifuge جهاز الطرد المركزى

الكواشف Reagent :

- حامض النيتريك (double distilled).

الطريقة:

- تنقع الأنابيب فى محلول عيارى HNO_3 2 N ليلا أو لعدة أيام.
- ثم تشطف بالماء المقطر و يفضل ان تترك لتجف ثم تحفظ فى اكياس بلاستيكية.
- ينقل 10 ميللى من العينة الى الانبوبة ويضاف HNO_3 5 ml of او 1 + 1 1 ml ($ml\ HNO_3$)

الى كلا من العينات والبلاك و المحاليل القياسية وكذلك عينات مراقبة الجودة.

يتم وضع الأنابيب فى السخان block heater وتضبط درجة الحرارة عند درجة حرارة 105° م مع وضع السدادات مع عدم إحكام الغلق .

- يتم هضم العينات لمدة ساعتين.
- يمكن إضافة كمية أخرى من حامض النيتريك المركز لاتمام هضم العينة الى ان يصبح محلول العينة فاتح اللون وشفاف.
- يترك الانابيب لتبرد ثم يكمل الحجم الى العلامة ويمزج جيدا.

- **ملحوظة:**

  - إذا كانت الأنابيب تحتوى على جزئيات فإنة يستخدم جهاز الطرد المركزى لفصل الرواسب ويتم نقل الراشح الى انبوبة أخرى.
  - يجب إحكام السدادة ويتم حفظها عند درجة حرارة 4درجة مئوية الى ان يتم تحليل العينة.

Standard Method (3030 F)

3 الهضم بإستخدام حامض النيتريك والهدروكلوريك Nitric acid hydrochloric acid digestion

- **الأجهزة المستخدمة : Apparatus:**
  - حمام مائى

الكواشف Reagent :

- **حامض النيتريك المركز ذو درجة نقاوة عالية.**
- **حامض الهيدروكلوريك (1+1).**
- **حامض النيتريك(1+1).**

الطريقة:

ا) حمض النيتريك- حمض الهيدروكلوريك Total HNO3/ HCl (A

- ينقل 100 ميللى من العينة (المعاملة بالحامض) الى قارورة او كأس ثم يضاف 3 ميللى من حامض النيتريك المركز وتغطى بزجاجة الساعة.
- يوضع الدورق على المسطح الساخن ويتم تبخير العينة الى اقل من 5 ميللى
- تبرد العينة وتشطف جدران الدورق وزجاجة الساعة بأقل كمية من الماء المقطر ثم يضاف 5 ميللى من حمض النيتريك المركز ثم يغطى الدورق بزجاجة الساعةوينقل نرة أخرى الى المسطح الساخن و ترفع درجة الحرارة.
- تستمر عملية التسخين ويمكن إضافة كمية من الحامض لإتمام عملية الهضم.
- يتم إضافة 10 ميللى من (HCl 1 +1) و 15 ميللى من الماء المقطر لكل 100 ميللى من الحجم النهائى المتوقع.
- وتستمر عملية التسخين ل 15 دقيقة أخرى لإذابة اى رواسب .
- يرشح المحلول و ينقل الراشح الى دورق معيارى سعة 100 ميللى و يكمل الى العلامة بالماء المقطر.

B) Recoverable HNO3/ HCl:

- ينقل 100 ميللى من العينة (المعاملة بالحامض) الى قارورة او كأس. **2 ml of (1+1 HNO3) و 10 ml of (1+1 HCl)** وتغطى بزجاجة الساعة.
- يتم التسخين بواسطة المسطح الساخن او بالحمام المائى حتى يختزل حجم العينة الى 25 مللى .
- تنقل العينة كميا الى دورق معيارى ثم يكمل الحجم الى العلامة ويمزج جيدا.

ج) طريقة الهضم بإستخدام حمض النيتريك – حمض الكبريتيك

Standard Method 3030 G

G) Nitric acid – Sulfuric acid digestion

الطريقة:

- ينقل 100 ميللى من العينة (المعاملة بالحامض) الى قارورة او كأس ثم يضاف 5 ميللى من حامض النيتريك المركز وتغطى بزجاجة الساعة.
- يوضع الدورق على المسطح الساخن ويتم تبخير العينة الى 15ميللى -20 ميللى ثم تترك لتبرد.
- ثم يضاف 5 ميللى من حامض النيتريك المركز و 10 ميللى من حامض الكبريتيك المركز:
- يتم تبخير العينة حتى تتصاعد الأبخرة البيضاء SO_3.
- يتم إضافة 10 ميللى من حمض النيتريك لاذابة الرواسب.
- يجب الخلص من حمض التيتريك تهائيا بواسطة التسخين المتمر حتى يصبح المحلول رائق وخاليا من الأبخرة البنية.
- تبرد العينة وبكمل الحجم الى 50 مللى

- يسخن المحلول الى درجة الغليان لاذابة الاملاح بطيئة الذوبان يتم ترشيح العينة اذا لزم الامر.
- ينقل الراشح الى دورق معيارى سعة 100 ميللى على مرتين ب 5 ميللى من الماء المقطر.
- يترك المحلول ليبرد ثم يكمل الحجم الى العلامة ويمزج جيدا.

الفصل الرابع

أجهزة القياس المختلفة

الفصل الرابع

أجهزه قياس المعادن

1- جهاز الإمتصاص الذرى

مقدمة:

Analytical method for determination of elements. طريقة لتحليل العناصر

It bases on the ability of free atoms to absorb electromagnetic irradiation. مبنى على قدرة الذرات الحرة لإمتصاص الإشعاع الكهرومغناطيسى

The sample solution is to be atomized. يتفتت محلول العينة

The atoms of the element to be determined are excited with light and heat تتم إثارة ذرات العنصر المراد تقديرة بالضوء والحرارة

The light absorption occurred in the sample (solution) is measured.

يتم قياس كمية الضوء الممتصة فى محلول العينة.

The absorption spectra of atoms are so called line spectra (the irradiation energy appears as very narrow lines).

تعرف طيف الإمتصاص للذرات الطيف الخطى (تظهر طاقة الإشعاع كخطوط ضيقة جدا)

The wavelengths used in AAS are the near-UV and the visible areas of spectra: about 190 nm —» 800 nm.

- تكون الاطياف المستخدمة فى جهاز الإمتصاص الذرى قريبة من منطقة الاشعة فوق البنفسجية و المنطقة المرئية : حوالى 190 نانوميتر الى 800 نانوميتر.

- Atoms and ions can absorb only light which has a certain frequency.

- تسطيع الأيونات والذرات إمتصاص الضوء الذى لة تردد معين.

- It is, they absorb light quantum of certain size, which is specific to the atom.

- تستطيع الأيونات والذرات إمتصاص كم من الضوء لة حجم معين يكون محددة لكل ذرة.

- That's why the light source used in the measurements is the emission source of the element to be determined.

- لذا يكون المدر الضوئى المستخدم فى القياسات مصدر انبعاث للعنصر المراد تقديرة.

- AAS-apparatus measures the amount of absorption and this is directly proportional to the free atoms which are in way of the light beam.

- يقيس جهاز الإمتصاص الذرى كمية الامتصاص والتى تتناسب طرديا مع الذرات الحرة التى تكون فى مسار الشعاع الضوئى.

- By comparing the absorbance of the unknown sample solution to the absorbance's obtained with standard solutions (using the same conditions) you can get the metal concentration of the sample solution.

- بمقارنة الامتصاص لمحلول عينة غيرمعلومة للامتصاص الناتج بواسطة المحاليل القاسية (تحت نفس الظروف) , يمكن الحصول على تركيز العنصر فى محلول العينة.

Different AAS- techniques used:

A. Flame technique : تقنية اللهب

- It converts the sample solution into an atomic vapour and then thermally elevates the atoms to an excited state.

- تتحول محلول العينة الى بخار ذرى وحينئذ تنقل الذرات بزيادة درجة الحرارة الى حالة الإثارة

- These atoms return to the ground state they emit light, which detected by the instruments

- عندما تعود هذة الذرات تعود مرة اخرى الى حالة الإستقرار فإنها تبعث ضوء ، يتم تقديرة بواسطة الجهاز.

- The intensity of light is related to the concentration of the elements in the solution.

- هناك علاقة بين شدة الضوء وتركيز العنصر فى المحلول.

- background corrector (D2-lamp) may be used if e.g. the flame has a very intensive colour

ربما يتم استخدام مصحح الخلفية (D2-lamp) اذا لوحظ كثافه لون اللهب.

- The measurements must be done within the linear scale.

- يجب ان تكون القياسات واقعة فى النطاق الخطى.

- Standards must be in the same solvent as the sample solutions.

- يجب ان يكون كلا من المحاليل القياسية محلول العينة محضرة فى نفس المذيب

- you may choose different wavelength (owing different sensitivity) according to the concentration of the sample

- يمكن يتم قياس العينة عند اطوال موجية مختلفة (تسبب حساسية مختلفة) تبعا لتركيز العينة.

- Air-acelylene flame about 2200 °C, suitable for most elements
- Nitrous oxide (N_2O-acetylene flame about 2600 °C, used for difficult atomizing elements like Sn, Al, Ba

B. Non flame techniques: تقنية غير لهب

a. Graphite furnace technique :تقنية فرن الجرافيت

- About 100 times as sensitive as flame technique but leads to risk of contamination.

- أكبر حساسية من تقنية اللهب 100 مرة.ولكن هناك احتمالية تلوث

- Atomization with heating electrically.

- يتم الإنقسام الذرى بالتسخين الحرارى.

- The graphite cylinder is heated by the passage of an electric current to the temperature, which is enough to evaporate the solvent from the solution.

- يتم تسخين اسطوانة الجرافيت بالتسخين بإمرار تيار كهربى الى درجة حرارة تكون كافية لتبخير المذيب من المحلول.

- The current is then increased so that firstly the sample is ashed and then it is vaporized and the metal atoms are produced.

- يتم زيادة التيار لكى تتحول العينة الى رماد ثم يتحول الى بخار ثم تتحول الى ذرات.

- Background correction necessary (D2 ,Zeeman).

- يجب استخدام مصحح للخلفية (D2 , Zeeman)

- Matrix modifiers and platform are used to eliminate interferences caused by matrices.

- يجب استخدام Matrix modifiers and platform للقضاء على التداخلات الناتجة من matrices

- Use the right temperature program, it can be tested by so called "cross curve", it is: to change the temperature in ashing and atomization stage.

- يجب إختيار برنامج حرارى مناسب ويمكن اختبارة بما يسمى "cross curve ويتضمن التغير فى درجة حرارة مرحلتى الترميد ومرحلة الانقسام الذرى.

B. Cold vapour technique (for Hg): تقنية البخار البارد (للزئبق)

- **Hydride generation method:**

- Elements (As, Se, Sb, Bi, Se, Te, Ge , Hg, and Pb) are difficult to analyze by flame AAS because it is difficult to reduce compounds of these elements especially those in higher oxidation state) to gaseous atomic state. The hydrides of arsenic, selenium, tellurium, antimony, bismuth and tin (and to lesser degree lead and germanium) are volatilized by the addition of reducing agent like sodium tetrahydroborate (III) to an acidified solution. Other systems have used titanium (III) chloride/magnesium powder and tin (II) chloride/potassium iodide/zinc powder as reducing agents.

يتم تحليل العناصر (As, Se, Sb) التى من الصعب تحليلها بواسطة جهاز الامتصاص الذرى المزود بوحدة الهب حيث يصعب إختزال مركبات هذة العناصر(وخاصة عندما تكون فى حالة اكسدة اعلى) الى الحالة الغازية الذرية. ربما تتحول هذة المركبات الى صورة الهيدريد المتطايرة وذلك بإستخدام sodium borohydride كعامل مختزل، وهى غير مستقرة عند درجات الحرارة المرتفعة حيث انها تنحل الهيدريد الى بخار ذرى بواسطة الحرارة.

- Sodium tetrahydroborate (III) is the preferred method because it gives faster hydride formation, higher conversion efficiency, lower blank levels and is more simple to use.

- يفضل استخدام (III) Sodium tetrahydroborate لانة يكون اسرع هيدريد واقل مستويات للبلانك وسهل الاستعمال.

- The principle of the hydride generation method is shown as follows using selenium as an example:

- Se^{4+} (Aq) + BH_4^- (aq) + $H^+ \rightarrow H_2$ Se (g) ↑ + H_2 (g)↑ + H_3BO_3

- H_2Se (g) → Se (g) + H (g)

- Mercury is reduced to the atomic form in a similar manner.

- After the gaseous hydride is formed it is passed, together with any excess hydrogen gas, to the atomizer mounted in the optical path of the spectrometer.

- بعد تكوين الهيدريد فانة يمر الى البخاخة atomizer الموجودة فى المسار الضوئى للسبكترومیتر.

- In case of As determination, the flame is required the flowing flames are suitable for use with the flame heated T-cell: Air/Acetylene, argon/hydrogen, air/ hydrogen, nitrogen/hydrogen. However, Nitrous oxide/acetylene and nitrous oxide/ hydrogen flames must never be used to heat the T- cell.

- فى حالة الزرنيخ ، يستلزم استخدام اللهب لتسخين ال T-cell , هواء- استيلين, ارجون-هيدروجين, هواء-هيدروجين , نيتروجين – هيدروجين. كيفما لايستعمل لهب غازات اكسيد النيتروز/ الاسيتيلين و أكسيد النيتروز / هيدروجين لتسخين T- cell

انواع اللمبات المستخدمة فى جهاز الإمتصاص الذرى(Lamps for AAS)

لمبة الكاثود المجوفة Hollow cathode lamp (HCL):

- Suitable for most elements (discharge lamp)

مناسبة لمعظم العناصر(لمبة مفرغة)

- The cathode is made about the element to be determined.

الكاثود مصنوع من العنصر المراد تقديرة

- For certain elements short-lived because of the volatilizing (e.g. As, Se). – قصيرة العمر لبعض العناصر بسبب التبخير (مثل ِ السيلنيوم الزرنيخ)

- Cheapness. رخيصة الثمن

Electrodeless discharge lamp (EDL):

- Longer durability for most elements.
- اطول فترة لمعظم العناصر
- Greater sensitivity and stability.
- أكثر حساسية واستقرار
- Need their own power supply.
- تحتاج الى مصدر للتيار خاص بها
- Expensive.مكلفة

Hollow Cathode Lamps

- Hollow cathode lamps are the most widely used radiation sources in the AA technique.

- مصدر للاشعاع اكثر استخداما فى تقنية الامتصاص الذرى.

- A hollow cathode lamp consists of a glass cylinder, and an anode and a cathode (Figure 18). The cylindrical cathode is either made of the analyte element or filled with it. The diameter of the cathode is 3 to 5 mm.

- تتكون من إسطوانة زجاجية و انود وكاثود. يتم صنع الكاثود اما من العنصر المراد تحليلة او يملىء بة.

- The anode is in the form of a thick wire and usually made of tungsten, nickel, tantalum, or zirconium.

- يكون الانود فى صورة سلك سميك و عادة مصنوع من التنجستين ، النيكل ،

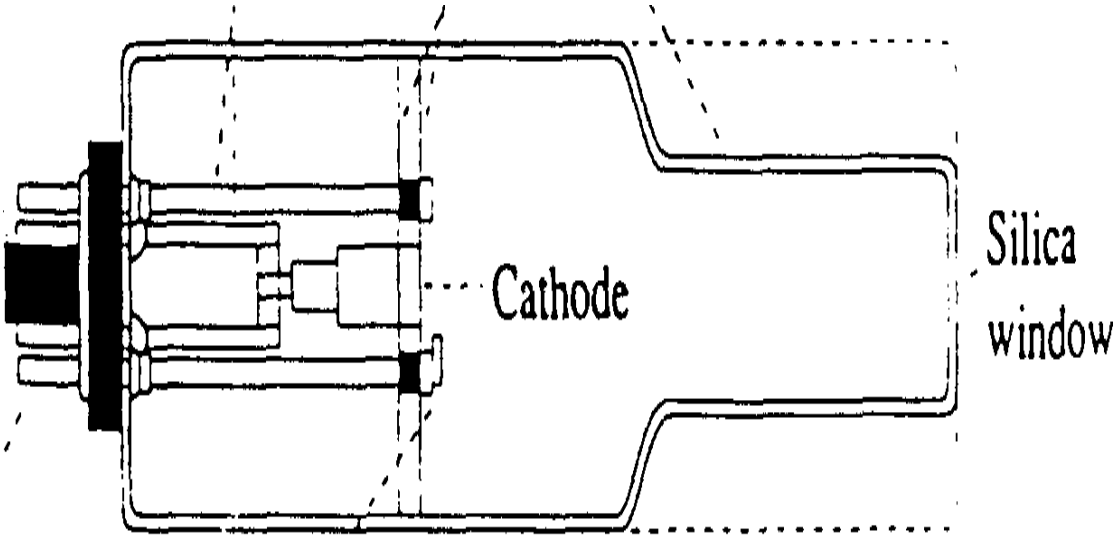
- The glass tube is first evacuated and then filled with an inert gas (argon or neon).

- تفرغ الانبوبة الزجاجية اولا ثم تملىء بغاز خامل (ارجون او نيون)

- The pressure of the inert gas is about 0.5 to 1.3 kPa.

يكون ضغط الغاز الخامل حوالى من (0.5 to 1.3 kPa).

Octal base plug Supports Mica shields Graded seal



Connecting pins Anode Glass envelope UV glass window

Construction of modem hollow cathode lamp (Philips Scientific)

Matrix modification in GFAAS:

To find the optimal parameters in measurements:

1) as high ashing temperature as possible

2) as low atomization " " "

- It is not always possible to use ashing temperature high enough without loss (vitalization) of the element.

- يمكن باستخدام matrix modifier استخدام درجة حرارة عالية للترميد بدون فقد (تبخير) للعنصر.

- **The idea in using matrix modifiers is:**

1) The volatilization of the element to be determined decreases and the great part of the matrix disappears.

يقلل عملية تبخير العنصر المراد تقديرة و يتخلص من جزء كبير من matrix او

2) The volatilization of the matrix increases and the disturbing compounds eliminate before the atomization of the element to be determined.

و يتم التخلص من المركبات المتداخلة قبل عملية الانقسام الذرى matrixزيادة تبخير ال للعنصر المراد تقديرة.

EXAMPLES

- As volatilizes at 200 °C, Ni is added —> Ni-arsenid decomposes >

1200 °C —> the ashing temperature may raised to 1200 °C

- high CI-concentration in the sample solution —> disturbances in

Pb and Cd measurements, add NH4H2P04 -> NH4Cl

AAS - ATOMIC ABSORPTION SPECTROMETRY (SCOPY)

- Atomic absorption is a process involving the absorption by free atoms of an element of light at a wavelength specific to that element or put, i.e. a means by which the concentration of metals can be measures.
- When a sample or sample solution is burned in a flame or heated in tube, the individual atoms of the sample are released to form a cloud inside the flame or tube.
- Each atom consists of a positively charged nucleus surrounded by a number of electrons in rapid motion around the nucleus.
- For each electron in each atom there is a discrete set of energy levels that electron can occupy.
- The spacing of the energy levels is different for each electron in the atom, but for similar corresponding electrons have identical spacing.
- For an unexcited atom, each electron is in the ground state. To excite the atom, one or more electron can be raised to the first or higher energy levels by absorption of energy by the atom. This energy can be supplied by photons or by collisions due to heat
- Those electrons furthest from the nucleus require least energy to go from the ground state E0 to the first energy level E1.
- The energy E corresponds to the energy gap between the ground state and the first energy level.

$$E = E1 - E0$$

- The energy required for this transition can be supplied by a photon of light with an energy given by:

  E= h ν, where h = Planck's constant and ν the frequency.

  This corresponds to a wavelength (λ) of (λ) = hc/E, Where c is the speed of light in vacuum.

- Metallic and metalloid elements, contain so called valence electrons which are relatively loosely bound to the nucleus and which can be excited by photons of wavelengths in the optical range 190 – 900 nm,

- For each atom of a metal or metalloid the energy gap is not found in any other element.

- If light of sufficiency narrow wavelength rage, centered on Hc / E1 - E0 is sent through a cloud of various atoms, only atoms of one particular element will absorb photons.

- Hence the selectively of the atomic absorption technique, atoms in the cloud move at high speed and collide with each other, and absorb over a narrow range of wavelengths.

- The width of a typical absorption line is about 0.001nm.

- For atomic absorption instrument purposes, an emission source with an emission line of the same frequency and a width of about 0.001 nm is normally used.

- This requirement is satisfied by an emission spectrum of the element of interest, generated by hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

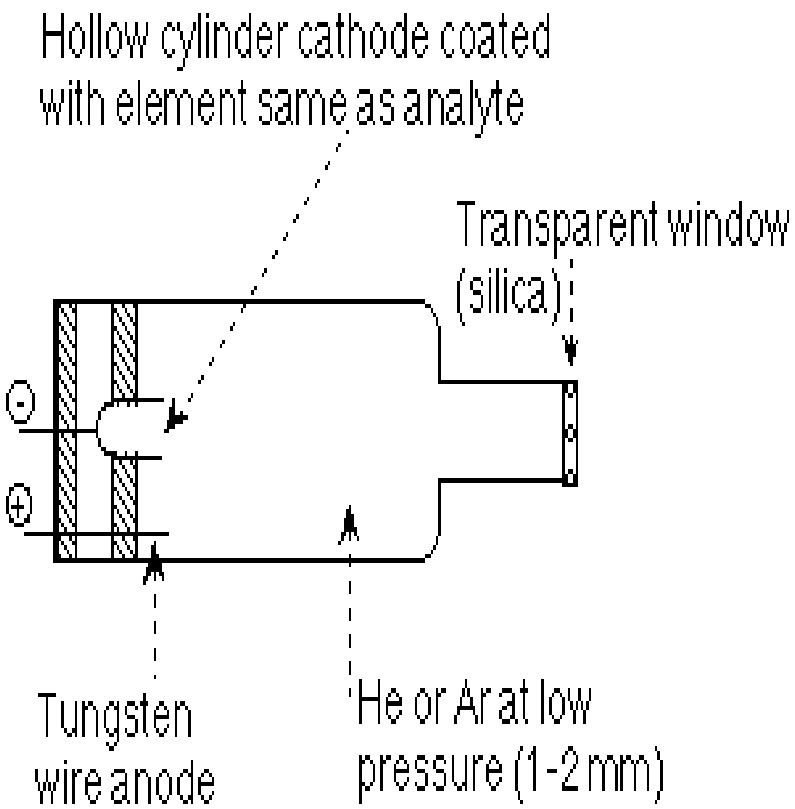
- That's why the light source used in the measurements is the emission source of the element to be determined

- AAS-apparatus measures the amount of absorption and this is directly proportional to the free atoms which are in way of the light beam
- By comparing the absorbance of the unknown sample solution to the absorbance obtained with standard solutions (using the same conditions) you can get the metal concentration of the sample solution.

There are three basic components for every AA spectrophotometer:

1. **Light source:**

It is designed to emit the atomic spectrum of a particular element. Specific lamps are selected according to the element to be determined. The hollow cathode lamp (HCL) or electrodes less lamps (EDL) are widely used.



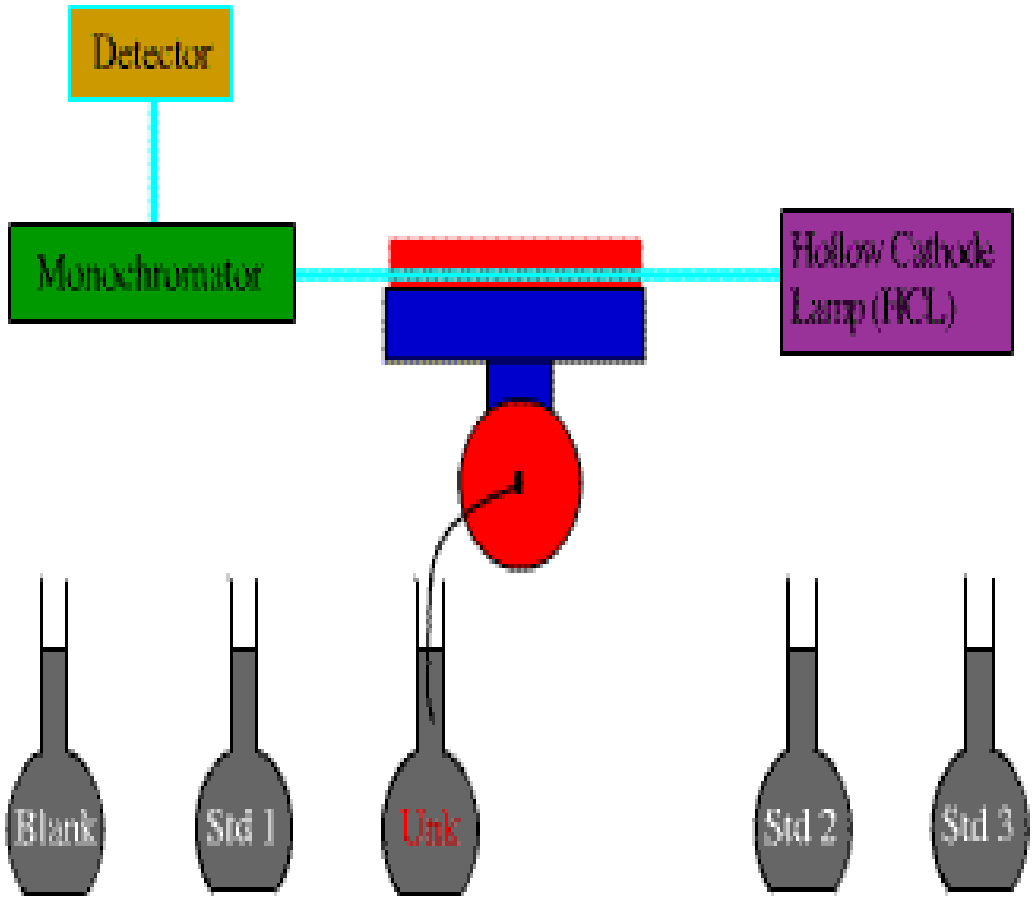
1) **Sample cell:**

Where an atomic sample vapor is generated in the light beam from the source. This is usually done by introducing the sample into a burner system (Flame AAS) or electrically heated furnace or platform, aligned in the optical path of the spectrophotometer.

3. Specific light measurement - Includes several components:

a) A monochromator to disperse several wavelengths of lights that are emitted from the light source to isolate a particular line of interest,

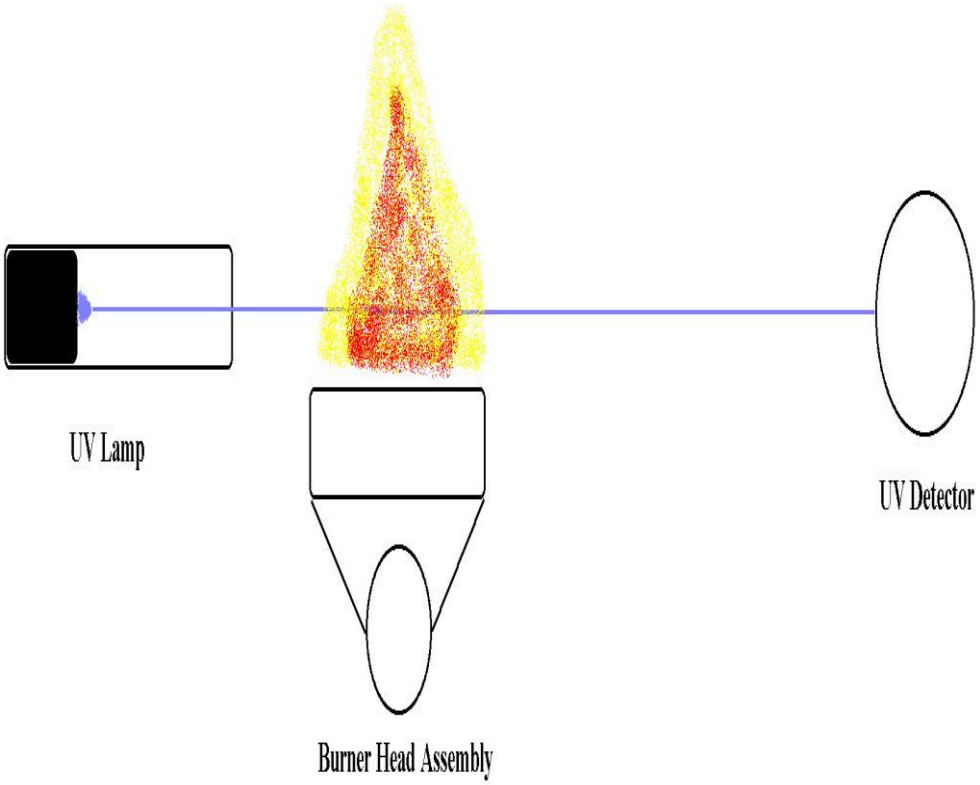
b) A detector to produce an electrical current that is dependent on the light intensity. This electrical current is amplified and processed by the instrument electronics to produce a signal, which is a measure of the light attenuation occurring in the sample cell and, this signal is further processed to generate an instrument readout in concentration units.

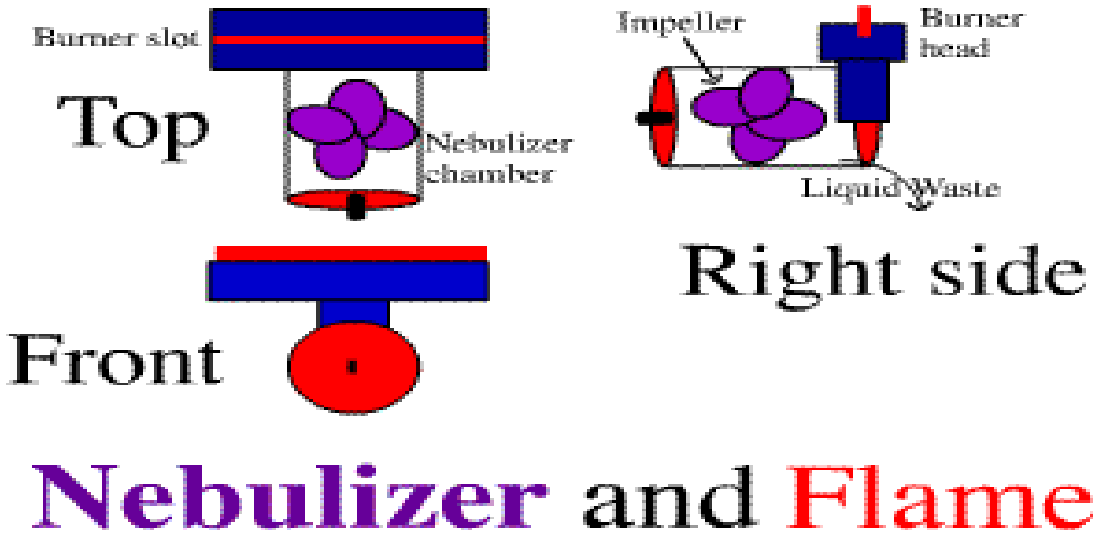

Detector
Monochromator
Hollow Cathode Lamp (HCL)
Blank
Std 1
Unk
Std 2
Std 3

Different AAS- techniques :

1) Flame technique :

- It converts the sample solution into an atomic vapour and then thermally elevates the atoms to an excited state.
- These atoms return to the ground state they emit light, which detected by the instruments
- The intensity of light is related to the concentration of the elements in the solution.
- Air-acelylene flame about 2200 °C
- Suitable for most elements
- Nitrous oxide (N2O-acetylene flame about 2600 °C
- Used for difficult atomizing elements like Sn, Al, Ba


UV Lamp
Burner Head Assembly
UV Detector



2) <u>Non flame techniques:</u>

a) <u>Graphite furnace technique:</u>

- Atomization with heating electrically
- About 100 times as sensitive as flame technique
- The graphite cylinder is heated by the passage of an electric current to the temperature, which is enough to evaporate the solvent from the solution
- The current is then increased so that firstly the sample is ashed and then it is vaporized and the metal atoms are produced in the solution.

Cold vapour technique (for Hg):

Hydride generation method:

- This technique makes use of the property that the metalloid elements (i.e As, Se, Sb, Bi, Se, Te, Ge , Hg, and Pb) exhibit, i.e. the formation of covalent, gaseous hydrides which are not very stable at high temperatures..
- The hydrides of arsenic, selenium, tellurium, antimony, bismuth and tin (and to lesser degree lead and germanium) are volatilized by the addition of reducing agent like sodium tetrahydroborate (III) to an acidified solution. Other systems have used titanium (III) chloride/magnesium powder and tin (II) chloride/potassium iodide/zinc powder as reducing agents.
- Sodium tetrahydroborate (III) is the preferred method because it gives faster hydride formation, higher conversion efficiency, lower blank levels and is more simple to use.

The principle of the hydride generation method is shown as follows using selenium as an example:

- Se4+ (Aq) + BH4- (aq) + H+ → H2 Se (g) ↑ + H 2 (g)↑ + H3 BO3
- H2Se (g) → Se (g) + H (g)
- Mercury is reduced to the atomic form in a similar manner
- After the gaseous hydride is formed it is passed, together with any excess hydrogen gas, to the atomizer mounted in the optical path of the spectrometer.

- In case of As determination, the flame is required the flowing flames are suitable for use with the flame heated T-cell: Air/Acetylene, argon/hydrogen, air/ hydrogen, nitrogen/hydrogen. However, Nitrous oxide/acetylene and nitrous oxide/ hydrogen flames must never be used to heat the T- cell.

Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS)

Introduction:

- Graphite furnace atomic absorption spectroscopy (GF-AAS) is a powerful technique suitable for trace analysis.
- The technique has high sensitivity.
- The ability to handle micro samples (5-100 ml) and a low noise level from the furnace.
- Matrix effects from components in the sample other than the analyte are more severe in this technique compared to flame-AAS.
- The precision is typically (5-10) % using GF-AAS

Principles:

- A graphite tube is located in the sample compartment of an AA spectrometer with the light from an external light source passing through it.
- A small volume of sample is placed inside the tube, which then is heated by applying a voltage across its ends.

- The analyte is dissociated from its chemical bonds and the fraction of analyte atoms in the ground state will absorb portions of light.
- The attenuation of the light beam is measured.
- As the analyte atoms are created and diffuse out of the tube, the absorption raises and falls in a peak-shaped signal.
- Beer-Lamberts law describes the relation between the measured attenuation and concentration of analyte.

GRAPHITE TUBES (FURNACES) TYPES

I. **Standard tube = normal graphite.**

II. **pyrolytically coated tube:**

- The sample disperses (scatters) more even
- The formation of carbides decreases
- The service life increases
- The atomic vapor doesn't go through the walls of tube.

III. **Tube with platform: (L'vov's platform)**

- Temperature more stable
- The speed of heating is great (for platform)
- It is usable for easily volatilizing elements

Things which effect to the service life of tube

- temperatures
- atomization time
- matrix quality (acids, solids)
- physico-chemical characters of matrix

MATRIC MODIFICATION IN GFAAS

- **To find the optimal parameters in measurements:**
  - as high ashing temperature as possible
  - as low atomization " " "
  - It is not always possible to use ashing temperature high enough
  - Without loss (volatilation) of the element
- **The idea in using matrix modifiers is:**
  - The volatilization of the element to be determined decreases and
  - The great part of the matrix disappears or
  - The vitalization of the matrix increases and the disturbing^
  - Compounds eliminate before the atomization of the element to be determined

EXAMPLES:

- As volatilizes at 200 °C, Ni is added —> Ni-arsenid decomposes >
- 1200 °C —> the ashing temperature may raised to 1200 °C
- high CI-concentration in the sample solution —> disturbances in
- Pb and Cd measurements, add NH4H2P04 -> NH4Cl

Interferences:

1. Spectral interference:

a) Background absorption:

- The narrow bandwidth of hollow cathode lamps make spectral overlap rare. That is, it is unlikely that an absorption line from one element will overlap with another.
- Molecular emission is much broader, so it is more likely that some molecular absorption band will overlap with an atomic line. This can result in artificially high absorption and an improperly high calculation for the concentration in the solution.
- Background absorption is non-specific attenuation of radiation at the analyte wavelength caused by matrix components.
- Enhanced matrix removal due to matrix modification may reduce background absorption.
- To compensate for background absorption, correction techniques such as continuous light source (D2-lamp), Zeeman or Smith-Hieftje should be used.

Three methods are typically used to correct for this:

a) 1. Zeeman correction :

A magnetic field is used to split the atomic line into two sidebands . These sidebands are close enough to the original wavelength to still overlap with molecular bands, but are far enough not to overlap with the atomic bands. The absorption in the presence and absence of a magnetic field can be compared, the difference being the atomic absorption of interest.

b) Smith-Hieftje correction :

The hollow cathode lamp is pulsed with high current, causing a larger atom population and self-absorption during the pulses. This self-absorption causes a broadening of the line and a reduction of the line intensity at the original wavelength.

c) Deuterium lamp correction :

- In this case, a separate source a deuterium lamp with broad emission is used to measure the background emission.
- The use of a separate lamp makes this method the least accurate, but its relative simplicity
- The fact that it is the oldest of the three, makes it the most commonly used method

2. Non-spectral interference (Matrix effect):

- Non-spectral interference arises when components of the sample matrix alter the vaporization behaviour of the particles that contains the analyte.

- To compensate for this kind of interference, method of standard addition can be used.
- Enhanced matrix removal by matrix modification or the use of a L´vov platform may also lead to a reduction of non-spectral interferences.

Instrumentation:

a) Atomic absorption spectrophotometer single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, equipment for flameless atomization (graphite furnace) and a suitable recorder or PC.

b) The wavelength range must be 190-800 nm.

c) Hollow cathode lamps for As, Cu, Cr, Ni, Pb and Zn. Single-element lamps are preferred, but multi-element lamps may be used if no spectral interference can occur. Electrodeless discharge lamps may be used if available.

d) Pyrolytically coated graphite tubes.

Setting up a temperature programme:

a) A temperature programme consists most commonly of four steps: Drying, pyrolysis, atomization and cleaning.

b) Drying step:

i. A quick ramp (5 s) to 15oC below the boiling point of the solvent. Then a slow ramp (25 s) to reach a temperature just above the solvents boiling point.

ii. This provides a gentle evaporation without sputtering.

iii. Hold the furnace at the selected temperature until drying is complete (5- 10 s).

iv. The drying time will vary with sample volume and salt content.

v. A purge gas flow of 250-300 ml min-1 is normally used.

Pyrolysis step:

i. A pyrolysis curve should be made to find the appropriate temperature to use in this step without losing any analyte.

ii. Consult the instrument manual for the procedure of making a pyrolysis curve.

iii. In a pyrolysis step a typical ramp will vary between 20-50 oC/s.

iv. Too steep ramp may cause sputtering. A purge gas flow of 250-300 ml min-1 is normally used.

c) Atomization step:

i. An atomization curve should be made to find the appropriate temperature to use in this step.

ii. Consult the instrument manual for the procedure of making an atomization curve.

iii. The lowest temperature that still gives maximum signal should be used in order to extend the lifetime of the graphite tube.

iv. Zero ramp time is used in this step. Gas stop during atomization is recommended.

d) <u>Cleaning step:</u>

i. A tube cleaning cycle after the analyte measurement should be done to remove any remains of sample and thereby avoid memory effects.

ii. A purge gas flow of 250-300 ml min-1 is normally used.

Instrument performance:

a) **The characteristic mass** (sometimes called sensitivity) is defined as: The absolute mass of an element that will absorb 1% of the incoming radiation. This equals a signal of 0.0044 absorbance units (AU).

b) The characteristic mass may be used as an indicator of instrument optimization.

c) Values of the characteristic masses are most often given in the instrument documentation.

d) Experimental values for comparison can be determined by measuring the absorbance signal (area) of a known mass of analyte and calculate using the following formula:

mo = Vs * Cs*0.0044 AU / observed peak area

mo: Characteristic mass (ng)

Vs: Standard volume injected (ml)

Cs : Standard concentration (ng ml-1)

Chemical modifiers:

a. In order to achieve better separation between analyte and matrix prior to atomization, a chemical modifier can be used.

b. The role of the modifier is most often to stabilise the analyte making higher temperatures in the pyrolysis step possible without any loss of analyte.

c. The concentration level of most modifier mixtures is usually in the ppm level.

d. The injection volume most often is in the 5-20 µl region.

e. The modifier mixture should be injected and dried prior to sample injection.

Table 4.17.6: Proposed instrument parameters.

	l, nm	slit	Drying temp	Pyrolysis temp	Atomization temp	Chemical modifier	Pyrolysis temp.	Atomization temp.
As	193.7	0.7	120	500	2300	$Pd(NO_3)_2^+$ $Mg(NO_3)_2$	1300	2300
Cd	228.8	0.7	120	350	1800			
Cr	357.9	0.7	120	1350	2660	$Mg(NO_3)_2$	1650	2500
Cu	324.7	0.7	120	900	2600			
Pb	217.0	0.7	120	550	2000	$(NH_4)_3PO_4$ or $La(NO_3)_2$	700	1800
Ni	232.0	0.2	120	1200	2600			
Zn	213.9	0.7	120	350	1800	$Mg(NO_3)_2$	700	1800

Sequence of analysis

a) Start the analysis with an “empty tube” run.

b) If a significant signal is obtained, a cleaning step (2650oC, 2-3 s) should be run repetitively to remove the remains in the tube.

c) If this is not sufficient, the graphite tube should be replaced.

d) The chemical modifier solution (if used) should be checked for contamination in a separate run.

e) The blank solution should be analysed to establish a blank level.

f) In addition to the blank standard, at least 3 standards should be selected to cover the linear range.

g) Repeat the analysis until good agreement between replicates and a linear calibration curve is obtained.

h) A quality control standard should be analyzed to verify the calibration.

i) Samples that are found to have concentration higher than the highest standard should be diluted into range and reanalyzed.

j) To monitor the performance of the graphite tube, a mid-level standard and a blank standard should be run after every 10th sample.

Flame atomic absorption spectroscopy (F-AAS)

Introduction

1. F-AAS is a very specific technique prone to few interference effects.

2. F-AAS is a single element technique with analyte determinations in the mg l-1 region as routine for most elements.

Principles

a) A liquid sample is nebulized to form a fine aerosol, which is mixed with fuel and oxidant gasses and carried into a flame.

b) In the flame the sample is dissociated into free ground state atoms.

c) A light beam from an external light source emitting specific wavelengths passes through the flame.

d) The wavelength is chosen to correspond with the absorption energy of the ground state atoms of the desired element.

e) The measured parameter in F-AAS is attenuation of light.

f) Lambert-Beers law expresses the relationship between the attenuation of light and concentration of analyte.

Interferences:

a) F-AAS is known as a technique with few problems related to interference effects.

b) The interferences that occur are well defined, as are the means of dealing with them.

c) For analysis of a few elements the type and temperature of the flame are critical; with improper conditions ionization and chemical interferences may occur.

Ionization:

a) Ionization of the analyte atoms in the flame depletes the levels of free ground state atoms available for light absorption.

b) This will reduce the atomic absorption at the resonance wavelength and lead to erroneous results.

c) The degree of ionization of a metal is strongly influenced by the presence of other invisible metals in the flame.

d) By addition of an excess of a very easily ionized element to the blanks, standards and samples the effect of ionization can usually be eliminated.

e) Ionisation is most common in hot flames such as nitrous oxide- acetylene flames.

f) In an acetylene-air flame ionization is most often limited to be a problem in analysis of the alkali- and alkaline earth metals.

1. Chemical interference:

a) The most common type of chemical interference occurs when the sample contains components that forms thermally stable compounds with the analyte and thus reduce the rate at which it is atomised.

b) Adding an excess of a compound that form thermally stable compounds with the interfering element eliminates chemical interference.

c) For example, calcium phosphate does not dissociate completely in the flame. Addition of Lanthanum will tie up the phosphate allowing calcium to be atomized.

d) A second approach to avoid chemical interference is, if possible, to use a hotter flame.

e) Using the method of standard addition can also control chemical interference.

2. Physical interference:

a) If the physical properties as viscosity and surface tension vary considerably between samples and standards, the

sample uptake rate or nebulization efficiency may be different and lead to erroneous results.

b) Dilution of samples or method of standard addition or both can be used to control these types of interferences. .

3. Background absorption and light scattering:

a) Matrix components that are not 100% atomised and that has broadband absorption spectra may absorb at the analytical wavelength.

b) Tiny solid particles in the flame may lead to scattering of the light over a wide wavelength region.

c) The background absorption can be accounted for by using background correction techniques such as continuous light source (D2-lamp) or Smith-Hieftje.

Instrumentation:

- Atomic absorption spectrophotometer single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, equipped with a air-acetylene burner head and a suitable recorder or PC.

- The wavelength range must be 190-800 nm.

Calibration standards:

- Calibration standards are prepared by single or multiple dilutions of the stock metal solution.

- Prepare a reagent blank and at least 3 calibration standards in graduated amount in the appropriate range of the linear part of the curve.

- The calibration standards must contain the same acid concentration as will result in the samples following processing.
- For precipitation samples, that would be 1% (v/v) HNO3 and for suspended particulate matter10% (v/v) HNO3.
- The calibration standard should be transferred to polyethylene bottles.

Instrumental procedure:

a) The operating procedure will vary between instrument brands, so the instrument manual should be followed carefully.

b) The position of observation and the fuel: oxidant ratio must be optimized.

c) Some general guidelines are outlined below

d) Light the hollow cathode lamp or electrode discharge lamp and D2-lamp if such background correction is used.

e) Set the lamp current to the value specified by the manufacturer.

f) Position the monocromator at wavelength 213.9 and choose slit with 0.7 and slit height “high”.

g) Carefully balance the intensity of the hollow cathode lamp and the D2-lamp if such background correction is used.

h) Align the burner head to assure that the centre of the light beam passes over the burner slot.

i) Light the flame and regulate the flow of fuel and oxidant to produce an oxidizing flame (lean blue).

j) Aspirate calibration blank and establish a zero point.

k) Aspirate standard solutions and construct a calibration curve.

l) Aspirate distilled water after each standard or sample.

Instrument performance:

The "characteristic concentration" (sometimes called sensitivity) is defined as the concentration of an element (mg l-1) that will absorb 1 % of the incoming radiation. This equals a signal of 0.0044 absorbance units (AU).

The "characteristic concentration" is instrument dependent and is calculated as follows:

Cm = (S * 0.0044 AU) / measured absorbance
C: Characteristic concentration (mg l-1)
S: Concentration of measured standard (mg l-1)

Cm Knowing the "characteristic concentration" allows the analyst to check if the instrument is correctly optimized and performing up to specifications.

Sequence of analysis:

- Aspirate calibration blank and establish a blank level
- Aspirate calibration blank and standard solutions and construct a calibration curve.
- Use at least 3 standard solutions in addition to the calibration blank to cover the linear range. Every point at

the calibration curve should, if possible, be based on replicate analysis.

- Distilled water should be aspirated after each standard and sample.
- A quality control standard should be analysed to verify the calibration.
- A calibration blank should be analysed to check for memory effects.
- Aspirate unknown samples.
- Aspirate a quality control standard for every 10th sample to check for drift.
- Samples that are found to have concentration higher than the highest standard should be diluted and reanalyzed.

Lamps for AAS:

1. Hollow cathode lamp (HCL):

a) Suitable for most elements (discharge lamp)

b) A hollow cathode lamp consists of a glass cylinder, and an anode and a cathode. The cylindrical cathode is either made of the analyte element or filled with it.

c) The anode is in the form of a thick wire and usually made of tungsten, nickel, tantalum, or zirconium.

d) The glass tube is first evacuated and then filled with an inert gas (argon or neon).

e) The pressure of the inert gas is about 0.5 to 1.3 kPa

f) for certain elements short-lived because of the volatilazion (e.g. As, Se)

g) cheapness

2.Electrode less discharge lamp (EDL):

1. longer durability for most elements greater sensitivity and stability
2. need their own power supply
3. expensive

Hydride Generation Analysis

- Hydride generation – elements which form gaseous hydrides: Sb, As, Bi, Se, Te, Sn - HGAAS
- Hg – Cold Vapour, CVAAS
- Acidified sample solution is reacted with NaBH4 producing the analyte hydride, which is carried on a stream of argon carrier gas to the atomizer
- The hydride decomposes in the atomizer to the elemental form and can be measured
- A number of elements such as arsenic and selenium form volatile hydrides on reduction of their salts with suitable reducing agents such as sodium borohydride.
- Atomic absorption of the free atoms of the analyte element then occurs in the same way as with the flame or with an electrically heated cell.
- Mercury can be determined in the same way but in this case the inorganic mecury present in the samples is reduced to atomic mercury, which can then be swept into the absorption tube where the atomic absorption process occurs
- This analysis the tube does not need to be heated as the free atoms are generated at room temperature.Hence the name Cold Vapour AAS.

The basic theory is that:

1. The acidified sample solution is reacted with NaBH4 producing the analyte hydride, which is carried on a stream of argon carrier gas to the atomizer.
2. The hydride decomposes in the atomizer to the elemental form and can be measured

Now for the science--------

1. Acidify sample
2. Mix with reluctant
3. Sodium borohydride NaBH4
4. Analyte reduced to gaseous hydride
5. As3+ + BH4- + H+ -> AsH3 (gas) + BO3 + H2
6. Gaseous analyte hydride separated from liquid reagents
7. Gas liquid separator device
8. Gaseous analyte hydride carried into heated cell
9. Inert (e.g. Ar, N2) used to transport it
10. Analyte atomised, and AA signal measured

Hydride V's Flame

Reasons for poor flame sensitivity for hydride group elements:

1. Low intensity HCL's
2. Absorption by flame gases
3. Inefficiencies in sample intro eg. Nebulisation
4. Improved sensitivity and reduced noise result in detection limits typically 1000x better than those achieved by conventional flame analysis.
5. The primary resonance lines used to measure the hydride group elements are in the deep UV region of the spectrum – indeed, the primary arsenic and selenium lines are below 200nm.
6. In this region of the spectrum, the normal flame gases, and even the air itself, will absorb a significant proportion of the radiation emitted by the lamp.
7. This combination of low intensity hollow cathode lamps and the absorption by the flame gases results in rather noisy absorption signals, and consequently poor detection limits.
8. Hydride generation offers the opportunity to improve sensitivity and reduce noise resulting in improved detection limits, which are typically 1000x better than those achieved by conventional flame AAS.

Vapour Generation - Modes of Operation

Vapour Generation accessories can be designed in 3 ways:

1. Batch Operation
2. Flow Injection
3. Continuous Flow

Batch Operation

a. Discrete portions of reagents are mixed with each sample
b. Volatile hydrides generated are swept into the spectrometer for measurement.
4. The signal is measured as a peak

Benefits:

i. The hardware required is cheap and simple.
ii. Detection limits can be good, as large volumes of sample can be used.
iii. No software interface is required.

Drawbacks:

1. Sample throughput rate is low.
2. It is next to impossible to automate the measurement.
3. It is extremely difficult to interface the device to an autosampler.
4. Reagent consumption is high.
5. 5. Significant operator skill and dexterity is required..

2.Flow Injection Operation:

a) A peristaltic pump is used to generate continuously flowing streams of reagents.

b) A 6 port valve and sampling loop are used to inject discrete portions of the sample into one of the reagent streams.

c) The reagent streams are mixed, and the volatile hydrides are separated in a gas liquid separator and transported to the spectrometer for measurement.

d) The signal is measured as a peak

3.Continuous Flow:

a) Reagents and sample are pumped to a reactor zone, where the chemical reaction takes place.

b) The volatile hydrides are separated from the reaction mixture in a gas-liquid separator, and transported to the spectrometer for measurements.

c) The signal rises to a steady state value, and can be integrated for as long as desired.

Benefits:

a) The hardware required is reasonably simple. Signal precision is good.

b) Fully automatic operation is possible eg. auto samplers. Sample throughput rate is moderate.

c) Reagent consumption is moderate.

Drawbacks:

a) Sensitivity is limited by maximum sample flow rate.

b) Significant (>10 seconds) stabilization and wash through times are necessary to avoid memory effects.

c) A software interface may be required.

d) The design of the gas liquid separator is critical, and must be optimised empirically.

Sample Preparation Issues:

a) Sample preparation is a key issue with hydride generation analyses.

b) Sample pre-reduction requirements can be divided, as you would expect into their respective groupings on the periodic table.

c) Group VI elements Se and Te always require prereduction to the tetravalent state, since the hexavalent oxidation state for both elements would result in no measurable signal by any configuration.

d) Group VI - Se and Te require pre-reduction adding /boiling solutions with HCl for ~10 mins

e) Group V (As,Sb and Bi) require pre-reduction

f) usually achieved using either Potassium Iodide or L-Cysteine

g) Mercury requires no special prereduction sample preparation,

h) But the actual reduction of mercury can take place through two reaction mechanisms:

i) Sodium Borohydride (NaBH4)

j) Stannous Chloride (SnCl2)

.

Inductively coupled plasma (ICP)

- An **inductively coupled plasma** (**ICP**) is a type of plasma source in which the energy is supplied by electrical currents which are produced by electromagnetic induction, that is, by time-varying magnetic fields.

    - **Plasma** refers to an ionized gas, in which a certain proportion of electrons are free, rather than being bound to an atom or molecule. The ability of the positive and negative charges to move somewhat independently makes the plasma electrically conductive so that it responds strongly to electromagnetic fields. Plasma therefore has properties quite unlike those of solids, liquids or gases and is considered to be a distinct state of matter. Plasma typically takes the form of neutral gas-like clouds (e.g. stars).

Operation:

- There are two types of ICP geometries: planar and cylindrical. In planar geometry, the electrode is a coil of flat metal wound like a spiral. In cylindrical geometry, it is like a helical spring.

- When a time-varying electric current is passed through the coil, it creates a time varying magnetic field around it, which in turn induces azimuthal electric currents in the rarefied gas, leading to break down and formation of plasma. Argon is one example of a commonly used rarefied gas.

- Plasma temperatures can range between 6 000 K and 10 000 K, comparable to the surface of the sun.

- ICP discharges are of relatively high electron density, on the order of 10^{15} cm^{-3}.
- As a result, ICP discharges have wide applications where a high density plasma is necessary.
- Another benefit of ICP discharges is that they are relatively free of contamination because the electrodes are completely outside the reaction chamber. In a capacitively coupled plasma (CCP), in contrast, the electrodes are often placed inside the reactor and are thus exposed to the plasma and subsequent reactive chemical species.

Applications:

- ICP-AES, a type of atomic emission spectrometry
- ICP-MS, a type of mass spectrometry.
- ICP-RIE, a type of reactive ion etching.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES):

Also, referred to as Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is an analytical technique used for the detection of trace metals.

It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element.

The intensity of this emission is indicative of the concentration of the element within the sample.

The ICP-OES is composed of two parts:

1. The ICP and
2. The optical spectrometer.

- The ICP torch consists of 3 concentric quartz glass tubes.
- A water cooled coil of a radio frequency (RF) generator which surrounds part of the torch.
- Argon gas is typically used to create the plasma.
- When the torch is turned on, an intense magnetic field from the radio frequency (RF) generator is turned on.
- The argon gas flowing through is ignited with a Tesla unit (typically a copper strip on the outside of the tube).
- The argon gas is ionized in this field and flows in a particular rotationally symmetrically pattern towards the magnetic field of the RF coil.

- A stable, high temperature plasma of about 7000K is then generated as the result of the inelastic collisions created between the neutral argon atoms and the charged particles
- Peristaltic pump delivers an aqueous or organic sample into a nebulizer where it is atomized and introduced directly inside the plasma flame.
- The sample immediately collides with the electrons and other charged ions in the plasma and is broken down into charged ions.
- The various molecules break up into their respective atoms which then lose electrons and recombine repeatedly in the plasma, giving off the characteristic wavelengths of the elements involved.
- A shear gas, typically nitrogen or dry compressed air is used to 'cut' the plasma flame at a specific spot. 1 or 2 transfer lenses are then used to focus the emitted light on a diffraction grating where it is separated into its component radiation in the optical spectrometer.
- The light intensity is then measured with a photomultiplier tube at the specific wavelength for each element line involved.
- The intensity of each line is then compared to previous measured intensities of known concentrations of the element and its concentration is then computed by extrapolation along the calibration line.

Practical part:

1. Calibration of the instruments and preparation of standard solutions.
2. Determination of 2 alkali (e.g. Na, K) metals and 2 heavy metals (Fe, Pb, Cr, Mn, Zn) in drinking water by Direct Air Acetylene method (standard method 3111B)
3. Determination of 4 heavy (e.g. Cd, Pb, Cr, Zn) in drinking water by Electrothermal Atomic Absorption method (standard method 3113B)
4. Determination of 2 heavy metals (e.g. Hg , Sn) in drinking water by Cold Vapour Atomic Absorption (standard method 3112 B)
5. Multiple determination of at least 10 element by ICP standard method 3120 B)

الفصل الخامس

التحقق من صحة النتائج

الفصل الخامس

التحقق من صحة النتائج

Quality Control

مقدمة:

مسئولية ضمان الجودة فى المعامل تنسب الي شخص له خبرة كافية ببرامج ضمان الجودة وكيفية أدارتة وتحديثه ولديه السلطة والمسئولية لتطبيق برنامج ضمان الجودة، وذو مركز يتيح له الاتصال بالإدارة العليا لنقل التقارير إليها. مسئول ضمان الجودة يجب أن تعليمه عمليا Technical education، مطلع على كل النواحي المعملية، وعلى علم بالطرق الإحصائية لتقييم النتائج. مسئول ضمان الجودة يقوم على إدخال البرنامج وتحديثها، إقناع الأعضاء بأهميته، وتقديم المعلومات الضرورية والتدريب لكل أعضاء المعمل.

تعريفات Definitions

- **حزمة الأستخلاص: Extraction Batch**

هي مجموعة من العينات الحقلية يتم أستخلاصها تحت نفس الظروف وبنفس الشخص خلال يوم عمل واحد ويستخدم محلول قياسي واحد لجميع العينات. وهذه المجموعة من العينات تحتاج الي عينات ضابطة

- **حزمة التحاليل:Analysis Batch**

عبارة عن مجموعة من العينات يتم تحليله تحت نفس الظروف خلال 24 ساعة متضمنة أختبار عملية المعايرة:Calibration check standards (CCC)

المحاليل القياسية: Standard Solutions

- **محلول قياسي مركز: Stock Standard Solution (SSS)**

محلول قياسي مركز يحتوي علي العنصر المراد قياسة في المعمل. ويمكن شرائة من جهات معتمدة وتركيزه غالبا 1000ملجم/ لتر

محلول قياسي أولي: Primary Dilution Standard (PDS) Solution

يحضر من المح لول المركزه Stock Standard Solution (SSS) ويخفف بالحمض المخفف الي تركيز متوسط مابين المركز والعياري. Calibration Standard (CAL)

- **محلول قياسي عياري: Calibration Standard (CAL)**

يحضر من المحلول القياسي الأولي(PDS) والعياري البديل (SUR) وذلك لمعايرة الجهاز وتحديد كفاءته وحساب تراكيز االعناصر المراد قياسها.

- **الضوابط: Blanks**

- **ضابط الكواشف المعملية:Laboratory Reagent Blank (LRB)**

يحضر للتعرف علي وجود أي شوائب أوتدخلات بالعينة خلال عملية تناول ومعالجة العينة. ويتم تحضيره بإختبار حجم من المياه الخالية من المعادن مساوي لحجم العينة المراد تحليلها ويتم التعامل معها كعينة.

إذا زاد تركيز العنصر المراد قياسة فى عينة البلانك عن حد التقدير لطريقة التحليل فإن هذا يشير الى وجود تلوث إما ان يكون ناتج من الكواشف أو من الادوات المستخدمة فى التحليل.

يجب تحليل عينة بلانك عند تحليل مجموعة من العينات (20عينة أو أقل).

ضابط للتأكد من جودة المعمل: Laboratory Fortified Blank (LFB)

يحضر بإضافة تركيز معلوم من العنصر المراد قياسة الي حجم من الماء الخالي من الملوثات المعادن (عينة بلانك) ويتم إجراء التحاليل الازمة كعينة تماما ، ويتم حساب معدل الإسترجاع ورسم control charts وحساب control limits للنتائج. ومن النتائج المتحصل عليها يمكن التعرف علي جودة ودفة التحاليل.

يجب تحليل عينة **(LFB)** عند تحليل مجموعة من العينات (20عينة أو أقل).

- **عينة حقلي مضاف اليه المكونات للتحقق من صحة النتائج: Laboratory Fortified Sample Matrix (LFSM**

عينة حقلية مضاف اليها العناصر المراد تحليلهاا Known quantities of the method analytes تحت نفس ظروف ومواصفات العينة . ويتم حساب معدل الإسترجاع ورسم control charts وحساب control limits للنتائج. ومن النتائج المتحصل عليها يمكن التعرف علي جودة ودفة التحاليل وذلك لتحديد كفاءة ودقة المعمل، مكونات العينة يجب قياسها واعتبارها القاعدة الأساسية عند الحساب.

يجب تحليل عينة **(LFSM)** عند تحليل مجموعة من العينات (20عينة أو أقل).

- **ضابط معملي مذدوج: Laboratory Fortified Sample Matrix Duplicate (LFSMD)**

تقسم عينة حقلية المضاف اليه العنصر للتحقق من صحة النتائج الي نصفين متساوين تماما، ويتم تحليلهما تحت نفس الظروف وبنفس الطريقة والمواصفات ومن نتائج التحاليل يمكن التأكد من صحة النتائج.

- **عينة مرجعية للتحقق من صحة النتائج: Quality Control Sample (QCS)**

تحضر في المعمل من المحاليل القياسية الأولية ويمكن الحصول عليها من جهات معتمدة.

خطوات التحقق من صحة النتائج Quality Control Procedure :

يجب علي المعامل المسئولة علي القيام بالتحاليل الخاصة بالعناصر الثقيلة اتباع برامج التحكم في جودة ودقة التحاليل بحيث تشتمل علي التقيم الأولي لقدرة المعامل، التأكد من أن كل حزمة تحاليل تشتمل علي جميع الضوابط والمحاليل العيارية والقياسية.

التقيم المبدئي للمختبر: Initial Demonstration of Capability (IDC)

. التقيم المبدئي للتعرف علي تركيز الشوائب:

Initial Demonstration of Low System Background:

للتأكد من خلو الكواشف من أي شوائب أو للتع رف علي التركيز المرجعي (background concentration) وذلك بتحليل عينة ضابط الكواشف المعملية Laboratory reagent blank والتأكد من خلو الكواشف من أي شوائب.

. التقيم المبدئي للجودة: Initial Demonstration of Accuracy

وذلك بتحليل عينة مرجعية معلومة التركيز ويجب أن تكون نتيجة التحليل مابين 80% الى 120% من التركيز الأصلي. بعد التاكد من التحاليل السابقة يتم تحليل عينة ضابط معملي تحتوي علي تركيز معلوم من أحد العناصر المراد قياسها أو أختيار تركيز متوسط مابين أعلي تركيز وأقل تركيز للمحاليل القياسية العيارية. ويجب أن يكون متوسط النتائج ± 20% من التركيز الأصلي.

التقيم ألاولي للدقة: Initial demonstration of accuracy

من النتائج المتحصل عليها في الفقرة السابقة (التقيم المبدئي للجودة) يتم حساب متوسط معدل الأنحراف Standard Deviation (SD) لجميع النتائج والفرق في معدل ألنحراف مابينتركيزين وعلي هذا الأساس يحسب معدل أنحراف النسبي ويشترط الايزيد عن 25%. يمكن تحليل عدد عينتيان معملية معلومة التركيز والقيا س بنفس الحسابات.

% RSD= (SD_1-SD_2) x100/ SD average

. تعين حد التقدير:(Detection Limit (DL:

يتم حسابة حد التقدير لكل عنصر كالاتى:

The DL for ech metal is calculated as DL= 3 x standard deviation of the mean of the blank determinations (n > 20).

ويعتبر حد التقدير غير ثابت حيث انة يحتاج الى إعادة تقيم من وقت لاخر تبعا للتغير فى مستوى الضابط المعملى (Blank)

. التحقق من جودة ودقة النتائج

1. **ضابط الكواشف المعملية:Laboratory Reagent Blank**

يتم القيام بتحليل عينة ضابط كواشف معملية مع كل حزمة التحاليل Analysis Batch وذلك للتأكد من خلو ها من أي شوائب أو للتعرف علي التركيز الموجود Back ground concentration نتيجة استخدام هذه الكواشف.

2. **اختبار المعايرة المستمر : Continuing Calibration Check (CCC)**

يتم بتحليل محلول قياسي عياري مع كل 20 عينة Analysis Batch بحيث يكون تركيزه يقع بمتوسط أقل تركيز وأعلي تركيز.

3. **إختبار الجودة بإستخدام محلول قياسي بديل Surrogate Standard (SUR)** .

يتم أضافة تركيز معين من المحلول القياسي البديل SUR الي العينة ومن نتائج التحليل يمكن تحديد الجودة وذلك بتطبيق المعاداة التالية:

$$R = \left(\frac{A}{B} \right) \times 100\%$$

Where

A = calculated surrogate concentration for the QC or Field Sample, and B = fortified concentration of the surrogate.

4. ضابط معملي مذدوج للتحقق من صحة النتائج وجودتها: (LFSMD)

تقسم عينة حقلية مضاف اليها المكونات المراد قياسها الي قسمين متساوين تماما، ويتم تحليلهما مع كل 20 عينة (Batch Analysis) تحت نفس الظروف وبنفس الطريقة والمواصفات ومن نتائج التحاليل يمكن التأكد من صحة النتائج وذلك بحساب الفرق النسبي بين النتيجتين.

$$RPD = \frac{|LFSM - LFSMD|}{(LFSM + LFSMD)/2} \times 100\ \%$$

يمكن حساب الفرق النسبي بتحليل عينتان حقليتنان من نفس الموقع وتحت نفس ظرف جمع العينات والتحاليل وذلك بتطبيق المعادلة التالية:

$$RPD = \frac{|FD1 - FD2|}{(FD1 + FD2)/2} \times 100\ \%$$

5. عينة مرجعية للتحقق من صحة النتائج: Quality Control Sample (QCS)

تحضر في المعمل من المحاليل القياسية الأولية ويمكن الحصول عليها من جهات معتمدة ويتم تحليلها ومن نتائج التحاليل يمكن حساب صحة وجودة النتائج لكل عنصر ويشترط أن تكون في حدود± 25 %.

المعايرة: Calibration

المحاليل القياسية العيارية

تحضر المحاليل القياسية العيارية عند تراكيز مختلفة لاتقل عن خمشة تراكيز ، وذلك بإضافة حجم معين من Stock standard solution 1000 mg/L الي قارورة عيارية سعة 100 مل تحتوي علي حمض مخفف مناسب (حمض نيتريك أو حمض هيدروكلوريك المخفف)، METB ثم التخفيف الي 100 مل.

المحلول العيارى الوسط ا: Intermediate standard solution (A)(100 mg/ml)

يتم ذلك بتخفيف 10مل من المحلول المركزة (Stock standard solution 1000 mg/L) و بنقل الى قارورة عيارية سعة 100مل تحتوي علي الحمض المخفف المناسب ثم التخفيف الي 100 مل.

المحلول العيارى الوسط (ب) Intermediate standard solution (10 mg/ml) (B)

يتم ذلك بتخفيف 10 مل من المحلول **Intermediate standard solution (A)(100 mg/ml)** الي قارورة عيارية سعة 100مل تحتوي علي الحمض المخفف المناسب ثم التخفيف الي 100 مل.

المحلول العيارى الوسط (ج) Intermediate standard solution (C)(1 mg/ml)

يتم ذلك بتخفيف 10 مل من المحلول **Intermediate standard solution (B)(10 mg/ml)** الي قارورة عيارية سعة 100مل تحتوي علي الحمض المخفف المناسب ثم التخفيف الي 100 مل.

محاليل العمل القياسية: Working standard solution

يتم تخفيف أحجام مختلفة من المحلول العيارى الوسط (ج) (1 mg/ml) الى قارورة عيارية سعة 100 مل ثم التخفيف الي 100 مل بحمض مخفف مناسب (حمض نيتريك أو حمض هيدروكلوريك المخفف) للحصول على تركيزات مختلفة لعمل المنحنى العيارى للعنصر المراد تقديرة.

الفصل السادس

تثبيت طريقة التحليل

الفصل السادس

تثبيت طريقة التحليل

Validation of analytical method

التثبت Validation:

تأكيد صحة القياس عن طريق الاختبار وتقديم أدلة موضوعية على أن متطلبات محددة قد تم تحقيقها

التثبت من صحة الطريقة Method Validation:

1. **عملية تبرهن خواص الأداء ومحددات استخدام الطريقة كما تعرف المؤثرات التي قد تغير هذه الخواص وإلى أي مدى بالإضافة إلى تحديد المقيس أو الخواص المقيسة داخل منظومة في وجود التداخلات والمؤثرات المحتملة. كما تبين درجة صحة النتائج ودقتها التي يمكن للطريقة تحقيقها في إطار ظروف خواص الأداء والمحددات والمؤثرات.**
2. **عملية تؤكد صلاحية الطريقة للغرض منها أي ملاءمتها لحل مشكلة معينة.**

متى يجب التثبت ؟:

- **عند إصدار طريقة جديدة لمعالجة مشكلة محددة.**
- **مراجعة طريقة تستخدم لتحسينها أو لتعالج مشكلة إضافية.**
- **إذا أظهرت إجراءات ضبط الجودة أن نتائج طريقة مستخدمة تتأثر بالوقت.**
- **عند استخدام الطريقة في معمل مختلف أو بواسطة أفراد آخرين أو باستخدام أجهزة مختلفة.**

لبيان تكافؤ طريقتان مثل طريقة جديدة ومواصفة قياسية للاختبار.

كيفية إختيار طرق التحليل:

- ملائمة للاختيار/المعايرة المطلوبة
- يفضل ان تكون منشورة في مواصفة دولية أو إقليمية أو وطنية
- أحدث الإصدارات السارية للمواصفة ما لم يكن ذلك غير مناسب أو غير ممكن.
- يمكن استخدام طرق طورها المعمل أو طرق يتبناها المعمل شريطة أن تكون مناسبة للغرض وتم التحقق من صحتها.
- فى حالة إستخدام طرق غير قياسية يجب التحقق من صحة الطريقة بالشكل المناسب قبل استخدامه.

وضع إجراءات طرق الاختبار أو المعايرة الجديدة قبل إجراء الاختبارات و/أو المعايرات حيث تحتوي هذه الطرق على المعلومات التالية على الأقل:

أ تعريف مناسب للطريقة و مجال عملها

ب وصف لطراز الغرض المراد اختباره أو معايرته

ج العناصر والكميات والمدى المراد تحديدها

د الأجهزة المستخدمة ومتطلبات الأداء الفني و مرجع القياس

هـ الظروف البيئية المطلوبة.

و وصف للطريقة يتضمن :

- المراجعات اللازمة قبل بدء العمل
- التحقق من أن المعدة تعمل بشكل صحيح قبل كل استخدام.
- طريقة تسجيل القراءات والنتائج
- أي إجراءات لضمان السلامة يجب مراعاتها.

- المقومات و/أو متطلبات القبول أو الرفض
- البيانات الواجب تسجيلها وطرق التحليل وعرض النتائج.
- اللايقين أو طريقة تقدير اللايقين.
- وضع علامات تمييز الغرض وتناوله ونقله وتخزينه وإعداده للقياس.

كيفية التحقق من صحة الطرق

- التحقق من صحة الطريقة هو التأكد بالفح ـص وتقديم الأدلة الموضوعية على أن الاحتياجات المعنية لتحقيق غرض محدد قد تم توفرها.
- على المعمل أن يتحقق من صحة الطرق الغير قياسية والطرق التي تم تصميمها / تطويرها بواسطة المعمل والطرق القياسية المستخدمة خارج المجال المراد لها والإسهاب أو التوسع والتعديلات التي قد يدخلها على الطرق القياسية وذلك للتأكد من صلاحية الطرق للغرض المقصود هذا ويلزم أن يكون التحقق شاملاً حسبما يجب لمواجهة احتياجات التطبيق ومجالاته . وعلى المعمل أن يسجل النتائج المستخرجة والطريقة المستخدمة للتحقق ونص يوضح ما إذا كانت الطريقة صالحة للغرض المقصود.
- يلزم أن يكون المدى وصحة القيم التي يحصل عليها المعمل من الطرق المحقق صحتها وثيق الصلة باحتياجات ال زبون للغرض المستخدمة من أجله هذه الطرق . ومن أمثلة المدى والقيم: قيمة اللايقين uncertainity في نتائج القياس وحدود الكشف وخطية النتائج وحدود التكرارية و/أو تطابق استخراجية النتائج وثباتها أمام المؤثرات الخارجية.

تقدير قيمة اللايقين في نتائج القياس:

- يجب تقدير قيمة اللايقين في نتائج القياس بشكل يمكن فهمه ويسهل استخدامه. يمكن الحصول على أغلب المعلومات المطلوبة لتقدير اللايقين أثناء إجراء عملية التثبت من صحة طرق القياس
- على معمل المعايرة أو معمل الاختبار الذي يجري المعايرات المراجعة الخاصة به أن يطبق طريقة لتقدير اللايقين في نتائج القياس لكل المعايرات

- **في حالات معينة تحول طبيعة طريقة الاختبار دون إجراء حسابات بالغة الدقة وصحيحة لقيم اللايقين في نتائج القياس يتعين على المعمل – على أقل تقدير – محاولة تعيين كل مكونات اللايقين وعمل تقدير معقول لقيمها.**
- **عند تقدير قيمة اللايقين في نتائج القياس يلزم أخذ كل مكونات اللايقين الهامة للحالة موضع الاعتبار مع استخدام طرق التحليل المناسبة.**

عناصر التثبت والمصطلحات

الاختبـــار Test:

عملية فنية تنتهي بتحديد خاصية أو أكثر لمنتج معين طبقا لطريقة محددة

معمل اختبـار Test Laboratory:

المعمل الذي يؤدي اختبارات ويمكن أن يكون المعمل كيان قانوني أو كيان فني أو كلاهما.

الغرض المختبر Test Item:

المادة أو المنتج المقدم للمعمل بغرض استخدامه في اختبارات الكفاءة الفنية.

طريقة الاختبـار Test Method:

طريقة فنية محددة لأداء الاختبار

نتيجة الاختبـار Test Result:

قيمة خاصية تم تعيينها بالكامل عن طريق طريقة قياس محددة

صحة (جهاز قياس) Accuracy:

قدرة جهاز القياس لإعطاء استجابة قريبة من القيمة الحقيقية

القيمـــة:

القيمة الحقيقية

True Value:

قيمة متوافقة مع تعريف كمية معينة (غير معروفة بالطبيعة).

القيمة الحقيقية المتفق عليها:

Conventional True Value (Assigned Value)

قيمة تنسب لكمية معينة وتقبل – أحيانا عرفيا – بقيمة لايقين مناسب لغرض معين.

القيمة المرجعية المقبولة

Accepted Reference Value :

القيمة المتفق على أن تمثل قيمة مرجعية للمقارنة وتشتق على أساس:

1. **مبادئ نظرية أو علمية**
2. **قيمة موثقة من عمل معملي قومي أو منظمة دولية**
3. **قيمة مجمع عليها نتيجة عمل معملي تعاوني**
4. **قيمة متوسطة لمجموعة محددة من القياسات**

اختبار كفاءة (المعمل) (Laboratory) proficiency testing:

تقييم أداء المعمل في الاختبارات عن طريق المقارنات بين المعملية.

المقارنات بين المعملية Interlaboratory comparisons :

عملية تنظيم وأداء وتقييم اختبارات تجرى على نفس الغرض المختبر أو مثيله بواسطة معملين أو أكثر طبقا لشروط محددة مسبقا.

في بعض الحالات قد يكون أحد المعامل المشاركة في برنامج المقارنات بين المعملية هو المعمل الذي يقدم القيمة الحقيقية المتفق عليها للغرض موضع الاختبار.

مادة مرجعية Reference material [RM]:

مادة ذات خاصية أو خواص متجانسة بشكل كافي ومثبتة بشكل جيد لتستخدم في معايرة جهاز أو تقييم طريقة قياس أو إعطاء قيمة متفق عليها لخواص المواد.

مادة مرجعية موثقة

Certified reference material (CRM):

مادة مرجعية مصحوبة بشهادة توثق قيمة خاصية أو خواص بطريقة تثبت الإسناد إلى تحقيق صحيح للوحدة التي يعبر عن الخاصية بها ويصاحب قيمة كل خاصية قيمة للايقين محددة بدرجة ثقة محددة.

معمل مرجعي Reference laboratory:

المعمل الذي يقدم القيم المرجعية للغرض المراد اختباره (مثال: معهد معايرة قومي)

التتبعية Traceability:

خاصية نتيجة قياس أو قيمة قياسية يمكن نسبها وإسنادها إلى قيمة مرجعية مقررة - عادة ماتكون قومية أو دولية – من خلال سلسلة متصلة من المقارنات ذات النتائج المصحوبة بقيم لايقين.

قوة (الطريقة): Robustness

قوة الطريقة التحليلية هي مقياس لقدرتها على البقاء دون التأثر بالتغيرات الصغيرة المتعمدة في عناصر الطريقة وتبين معولية استخدامها في الظروف المعتادة.

اختبار معولية (الطريقة): Ruggedness Test:

دراسة معملية لبحث سير عملية تحليلية عند إحداث تغيرات صغيرة في الظروف البيئية و/أو ظروف التشغيل مماثلة لما قد يحدث في ظروف مختلفة للاختبار. ويتيح اختبار المعولية الحصول السريع والمنهجي على معلومات عن تأثير التغيرات البسيطة.

القيمة البعيدة : Outlier

قيمة غير متوافقة مع باقي القيم المنتمية إلى نفس المجموعة

نتيجة متطرفة: Extreme results

القيم البعيدة والقيم الأخرى الغير متوافقة بشكل كبير مع القيم الأخرى المنتمية لنفس مجموعة البيانات. وقد يكون لهذه النتائج تأثيرا عميقا على الخواص الإحصائية مثل المتوسط الحسابي والانحراف المعياري.

التقنيات الإحصائية الفعالة:Robust statistical techniques

تقنيات لتقليل تأثير النتائج المتطرفة على تقدير قيم المتوسط الحسابي والإنحراف المعياري. وتستخدم هذه الأساليب لتقليل وزن النتائج المتطرفة بدلا من حذف هذه النتائج من مجموعة البيانات.

التكـراريــة : Repeatability

هى الدقــة تحت ظـروف متكـررة ، بمعنى الظـروف التي يمكن أن تعطى نتائج اختبار مستقل باستخدام نفس الطريقة على غرض مراد اختباره مماثل تماما في نفس المعمل بواسطة نفس الشخص مستخـدما نفس الأدوات خلال فترة زمنية قصيرة.

تكـراريــة (نتائج القياس) : Repeatability

مدى قـرب الاتفـاق بين نتائـج عمليـات قيـاس متتـابعة لنفس المقيس تمت تحت نفس ظروف القياس.

تكـراريــة (جهاز القياس) : Repeatability

قدرة جهـاز القيــاس على إعطـاء نتائـج متماثلة عند تكرار قياس نفس المقيس تحت نفس ظروف القياس.

تكـراريــة النتاج: Reproducibility

هى الدقة تحت ظروف إنتــاج متكررة، بمعنى الظـروف التي يمكن أن تعطى نتائج اختبار باستخدام نفس الطريقة على غرض مراد اختباره مماثل تماما في معامل مختلفـة بواسطة أشخاص مختلفين باستخدام أدوات مختلفة. ويلاحـظ أن النص الـدال على تكـرارية النتـاج يجب أن يتضمن تحديد الظروف التي تغيرت.

اللايقين فى القياس Uncertainty of measurement:

هو قيمة مرتبطة بنتيجة القياس تحدد مدى تشتت القيم التي يمكن أن تميز أو تنسب إلى المقيس.

اللايقين المعياري$u(x_i)$ Standard Uncertainty :

اللايقين في نتيجـة قيـاس معبـر عنـه بقيمـة انحـراف معياري واحد.

اللايقين المعياري المجمع :Combined Standard Uncertainty uc(y):

اللايقين المعياري لنتيجة القياس عندما نحصل على النتيجة من قيم لعدد من الكميات ، وتساوي القيمة الموجبة للجذر التربيعي لمجموع مربعات أطراف حيث يعرف الطرف بأنه قيمة تعبر عن تفاوت أو اختلاف قيم هذه الكميات بعد تحديد ثقل تأثير هذه الكميات على تغيرنتيجة القياس تبعا لهذه الكميات.

اللايقين الموسع: Expanded Uncertainty U

ه و كمية تحدد مدى لنتيجة قياس يتوقع أن يحصر نسبة كبيرة من توزيع القيم التي يمكن نسبتها للمقيس.

معامل التغطية أو الامتداد: Coverage factor k

ه و معامل عددي يستخدم لمضاعفة قيمة اللايقين المعياري المجمع للحصول على قيمة اللايقين الموسع. وعادة ما تكون قيمة هذا المعامل بين 2 و 3.

أدوات التحقــق

اختبارات الكفاءة Proficiency testing (PT)

اختبار الكفاءة (للمعمل): (Laboratory) proficiency testing

هو قياس لكفاءة أداء المعمل من خلال المقارنات البين معملية (دليل الأيزو 2)

المقارنات البين معملية: Interlaboratory comparisons

عملية تنظيم وأداء وتقييم اختبارات على نفس الغرض أو مثيله تتم فب معملين أو أكثر طبقا لشروط موضوعة مسبقا.

مع ملاحظة أنه في بعض الحــالات يكــون أحد المعامل هو المعمل الذي يعطي القيمة الحقيقيــة المتفق عليها للغرض أو الخاصية تحت الاختبار assigned value for the test item.

1- اختبارات الكفاءة بنظام القياس المقارن PT Measurement comparison schemes:

يتضمن هذا النظام تمرير الغرض المراد اختباره من معمل للمعمل التالى على التتابع

2- اختبارات الكفاءة بنظام المقارنات البين معملية PT Interlaboratory testing schemes:

يتضمن هذا النظام توزيع عشوائى متزامن لعينات فرعية من عينة واحدة على المعامل المشاركة للاختبار المتزامن.

3- اختبارات الكفاءة بنظام العينات المجزأة:PT Split-sample testing schemes

يتضمن هذا النظام مقارنة بيانــات عــدد صغيــر من المعامل (غالبا معملين) تحت التقييم كمعامل تقدم خدمة الاختبار.

4- اختبارات الكفاءة الوصفية PT Qualitative schemes

تقييم أداء معمل اختبار وقدراته على توصيف وجود أو كائن معين مثل توصيف نوع الأسبستس أو توصيف كائن حى مسبب للمرض ولهذا يكتسب نظام اختبار الكفاءة الصفة الوصفية.

5- اختبارات الكفاءة بنظام القيمة المعلومة PT Known – value schemes:

تتضمن بعض نظم اختبارات الكفاءة إعداد أغراض للاختبار ذات قيمة معلومة للمقيس ومن ثم يمكن تقييم قدرة معمل ما على اختبار غرض ومقارنة نتائجه بالقيمة الحقيقية المتفق عليها. هذا النوع من اختبارات الكفاءة لايتطلب اشتراك عدد كبير من المعامل.

6- اختبارات الكفاءة بنظام العمليات الجزئية PT Partial-process schemes :

تتضمن هذه النوعية الخاصة من نظم اختبارات الكفاءة تقييم قدرة المعامل على أداء جزء من اختبار شامل أو عملية قياس كلية.

أمثلة:

المعامل التي تقوم بتحليل وتحويل

البيانات وتصدر تقرير بدلا من إجراء

الاختبار أو القياس الفعلي .

المعامل التي تعد العينات طبقا لمواصفات محددة.

مراجع القياس

Measurement Standards

1. يستخدم مصطلح "مراجع القياس" لوصف مواد أو أدوات تستخدم للمعايرة أو توصيف خواص محددة.
2. تقليديا يستخدم هذا المصطلح لتسمية محاليل المادة الواحدة أما عمليا فيستخدم هذا المصطلح لتسمية أي أداة تستعمل في المعايرة لقياس عنصر معين أو توصيف خاصية محددة.
3. تشمل المراجع الأدوات التي يمكن أن تستخدم لمعايرة مدى لكميات فيزيائية (مثل الترمومتر المعاير على مدى درجات حرارة). وهنا تسمى هذه المراجع بمراجع القياس الفيزيائية.

III المواد المرجعية والمرجعية الموثقة

Reference Materials (RM&CRM)

المواد المرجعية: يمكن أن تكون أي مواد تستخدم كأساس لمرجع ويمكن أن تتضمن الكواشف المعملية معلومة النقاوة والكيماويات الصناعية أو مواد صناعية أخرى. ويلزم أن تكون الخاصية المرجعية مستقرة وثابتة زمنيا ومتجانسة في حين أن المادة المرجعية لاتحتاج درجة عالية من التوصيف والإسناد المترولوجي والتوثيق المماثل للمواد المرجعية الموثقة.

المواد المرجعية الموثقة: يكون توصيف الخاصية موضع الاختبار أكثر تشددا ودقة في هذه المواد بالإضافة إلى وجوب التصديق على قيمة الخاصية بشهادة من جهة معترف بها تحمل قيمة اللايقين المصاحبة لقيمة الخاصية موضع الاعتبار.

يتم التوصيف عادة باستخدام طرق مختلفة متعددة بحيث يمكن – بقدر الإمكان – تقليل أو حذف أي حيود أو انحياز في عملية التوصيف.

Blanks, Samples/Test Materials, Fortified Materials/Solutions, Spiked Materials, Incurred Materials and Independently Characterized Materials

1. استخدام أنواع مختلفة من المذيبات والعينات ومواد الاختبار ...الخ يتيح تقدير إلى أى مدى يمكن أن تنسب نتيجة القياس للمقيس أو لأسباب أخرى.
2. مواد الاختبار المأخوذة من عينات حقيقية تفيد في توفير المعلومات عن تأثير تداخل عوامل أخرى واقعية نواجهها في العمل اليومي.
3. من الصعب معرفة انحياز أو حيود نتائج طريقة بدون معرفة المكونات الحقيقية للمادة المختبرة. وإذا كانت مادة ما قد تم تحديد خواصها بوسائل أخرى (مثل استخدام طريقة يمكن إهمال انحيازها) فإنه يمكن استخدام تلك المادة كمادة مرجعية ومن ثم يمكن من خلال فحص نتائج الطريقة قيد التحقق تقييم انحياز الطريقة مقارنة بخاصية المادة المرجعية.

النسخ المطابقة Replicates

1. إذا استخدمت جيدا فإنها تعطي القائم بالقياسات والتحاليل المزيد من المعلومات الإحصائية الضمنية الخاصة بعملية قياس محددة.
2. يجب تصميم التجارب التي تستخدم نسخ متطابقة بحيث تأخذ في الاعتبار كل التغيرات في ظروف التشغيل المتوقع حدوثها خلال الاستعمال الروتيني لطريقة القياس أو التحليل
3. الهدف هو تحديد التغيرات الواقعية وليس الحد من حدوث تلك التغيرات.

الاستخدام والتوثيق

استخدام الطرق المحققة

عند استخدام طريقة محققة يجب اتباع القواعد العامة التالية للوصول للأداء المقبول:

1. **على فريق العمل المنوط به استعمال الطريقة أن يعكف على التعرف على العناصر المكونة من أجهزة ومواد وظروف بيئية وخطوات واحتياطات ففية واجبة بشكل جيد قبل العمل بها لأول مرة ويستحسن أن توضح خطوات الطريقة ببيان عملي من خبير بالطريقة.**

2. **تستخدم الطريقة في بادئ الأمر تحت إشراف مباشر ولصيق باستخدام عينات تجريبية أو مواد مرجعية على أن يتدرج تطبيق الطريقة تحت إشراف عن بعد حتى يصل فريق العمل إلى الثقة الكافية لأداء العمل بدون إشراف كعمل روتيني.**

3. **وفي جميع الأحوال عليك أن تتعرف بإمعان على الطريقة وتدرس الأساس النظري لعملية القياس أو التحليل وتتدرب على مراحل تنفيذه لتحديد أين يمكن التوقف ومتى يمكن استئناف القياس ومتى لا يجب التوقف.**

4. **كما يجب التقدير الجيد لعدد العينات أو الأجهزة المراد اختبارها في عملية القياس الواحدة فمن الأفضل التعامل مع عدد مناسب عند إجراء القياس أو الاختبار.**

5. **ومن نوافل القول أن نوصيك بالتخطيط والتحضير المسبق لكل ما يلزم لتنفيذ الطريقة قبل البدء.**

6. **إذا كان من الضروري أن تكيف أو تغير طريقة معمل آخر محققة فإنه لابد من إعادة التحقق من صحة الطريقة بعد التكييف أو التغيير. ويتوقف الحكم على نتائج التحقق من صحة الطريقة الأصلية تبعا لطبيعة التغييرات التي أدخلت على الطريقة.**

توثيق الطرق المحققة لماذا ؟

من الأهميـة بمكـان أن توثق الطريقة بعد أن يتم التحقق من صحة نتائجها ليتحقق التالي:

- **تنفيذ الطريقة بوضوح وبدون التباس.**
- **استخدام الطريقة طبقا لنفس الخطوات كل مرة.**
- **الحد من مدى حدوث تغييرات عارضة على الطريقة.**
- **كفاءة أداء المراجعات على الطريقة وأغراض التقييم.**
- **تلبية احتياجات الأغراض التعاقدية أو التشريعية.**
- **معرفة تأثير الطريقة على تكرارية نتاجها والتقدير المتوقع للايقين المصاحب للنتائج.**

توثيق الطرق المحققة ، كيف ؟

- **يجب أن تكتب المعلومات بالترتيب الذي يتوقع أن يحتاجه مستخدم الطريقة الموثقة.**
- **من المفيد عند اختبار جـودة توثيق الطريقــة أن ينفذ الخطوات الموثقة شخص كفؤ كما تنـص عليها الطريقة حرفيا.**
- **رغـم أنـه مـن المستحسـن أن تكـون كـل الطـرق موثقة طبقا لنموذج أو شكل عام موحـد إلا أنه من المعمـول به أيضـا ألا تعـطي كـل الطـرق نفـس الـدرجـة من التفـاصيـل وكثيـرا ما يكـون ملائـمـا حذف بعض الأجزاء من الوثيقة.**
- **تكـون الطـرق المـوثقـة جـزءا هـاما مـن نظـام الإدارة بالمعمل ومن ثم يجب أن تخضـع لدرجةمناسبة للسيطرة والتحكم.**
- **يجب أن تحتوي الطرق الموثقة على المعلومـات التي تمكن المستخدم من معرفة ما إذا كانت الطريقة اعتمدت للاستخدام وما إذا كانت كاملة. كما يجب أن تحمل الطريقة رقم الإصدار وتاريخه وإسم المـؤلف وعدد النسخ المطبوعة وأى قيود على نسخها.**
- **قد تحتاج الطريقة إلى التحديث من وقت لآخر وعندها يجب ألا يقوم بإجراء هذا التحديث أو التعديلات إلا الأشخاص المخولين سلطة ذلك.**

اللايقينUncertainity

1- مصادر اللايقين:

يجب أن يعرفها خبراء القياس كل في مجال تخصصه من واقع فهمهم لنظم القياس.

المعرفة المنقوصة لنظم القياس قد تؤدي إلى نتائج تبدو معقولة ولكنها غير صحيحة

المعايرات الكيميائية:

- **اللايقين الوارد في شهادات معايرة المعايير المرجعية**
- **اللايقين في أحجام ملئ قنينة القياس**
- **تأثير الظروف البيئية في قياسات الحجوم والأوزان**
- **تكرارية أجهزة القياس (أوزان – حجوم)**
- **اللايقين في نقاوة المواد المرجعية**

اللايقين في تركيز المحاليل العيارية

العوامل المشتركة:

1. **اللايقين الوارد في شهادات معايرة المعايير المرجعية**
2. **تأثير الظروف البيئية**
3. **تكرارية جهاز القياس**
4. **الأخطاء الرياضية**

التقريب والفروض (ط)

الجداول القياسية / توفيق المنحنيات

أخطاء التقريب

مثال: 3ر346 ← 3ر35 ← 3ر4

ولكن: 3ر346 ← 3ر3

الثبات مع الزمن

الملخـــص:

1. **تتوقف المصادر على المجال وإن كان هناك عوامل مشتركة**
2. **يلزم أخذها جميعا في الاعتبار حتى ولو لبيان عدم تأثير بعضها**
3. **قد تعتمد على طريقة معالجة البيانات**

التصنيـــف

طـــرز الـلايـقـيـن:

- **طراز A**
- **طراز B**

- **تقدير طراز A :**

يتم بالحسابات من سلسلة من الملاحظات المتكررة باستخدام الطرق الإحصائية.

- **تقدير طراز B:**

يتم بطرق أخرى غير الطرق المستخدمة في تقدير **الطراز A**

العوامل الداخلة في تقديرطراز B:

- **البيانات في شهادات المعايرة**
- **بيانات (نتائج) قياسات سابقة**
- **الخبرة والمعلومات العامة**
- **قيم مقبولة لثوابت معينة**
- **مواصفات الشركة المصنعة**
- **أى معلومات ذات صلة بالعملية**

- **طراز A , طراز B**

يمكن التعبير عن كلاهما كانحراف معياري باستخدام معامل مناسب يعتمد على توزيع احتمالي مفترض .

تجميـــع مكونـــات الـــلايـقـيـين

في تقييم مكونات اللايقين يلزم –على الأقل- أخذ مصادر الأخطاء المحتملة التالية في الاعتبار:

- **قيمة اللايقين المعطاة لمرجع القياس وأي انسياق (التغير البطيء في قيمة اللايقين أو قراءات المرجع) Drift أو أي عدم ثبات Instability في قراءات المرجع.**
- **الأجهزة المستخدمة في المعايرة أو القياسات بما في ذلك بعض المكونات لنظام القياس المستخدم التي يمكن أن تؤثر على قراءات نظام القياس مثل كابلات التوصيل.**
- **الأجهزة قيد المعايرة أو القياس (على سبيل المثال قوة التحليل والتغير البطيء في قيمة القراءات أو عدم ثبات في قراءات الجهاز أثناء معايرته)**
- **طريقة التشغيل Operational Procedure.**
- **تأثير الظروف البيئية على أي من أو كل العوامل السابقة.**

الجمع الحسابي والتعبير بقيمة المجموع الحسابي عن قيمة اللايقين الكلية:

- **من أسهل الطرق وأكثرها وضوحا لتجميع مقادير اللايقين المساهمة في قيمة اللايقين الكلية**
- **يمتاز بالسرعة والسهولة وإضفاء مستوى عال من الثقة بشكل عام**
- **بالنظرة الأولى انطباعا بدرجة ثقة تبلغ 100 % في مدى قيمة اللايقين الكلية في نتائج القياس.**

لم تعد مقبولة الآن لما لها من عيوب

أول هذه العيوب:

أنه من غير المرجح عند تجميع الأخطاء الناشئة من مصادر مختلفة مؤثرة على نتائج عملية القياس أن تكون مقاديرها وإشارتها الحسابية (سالبة أو موجبة) بحيث تضاف هذه المقادير إلى بعضها البعض لتصل إلى القيمة العظمى الحدية بما يعني الحصول – على نحو غير ملائم وبشكل دائم – على تقدير متشائم لقيمةاللايقين المحسوبة.

ثانى هذه العيوب:

ومن ثم فإنه بالتبعية إذا أضيفت النتائج المستبعدة بالحدس إلى مدى النتائج المحتوية على المصادر الأخرى للأخطاء فإن هناك احتمالا ضئيلا أن تقع "القيمة الحقيقية" للكمية المقاسة خارج قيمة اللايقين المذكورة. وبمعنى آخر فإن نسبة الثقة (100 %) المفترض الوصول إليها عن طريق المجموع الحسابي لمكونات اللايقين لا يمكن تحقيقها.وبالتالي فإن استخدام المجموع الحسابي لا يمكن معه تحديد درجة (نسبة) ثقة في أن "القيمة الحقيقية" للكمية المقاسة تقع داخل حدود قيمة اللايقين المذكورة.

الطرق الإحصائية:

ليست طرق مثالية، حيث تعتمد أحيانا على أنواع من التوزيع الاحتمالي الغير مثالي للحصول على خ ـواص معينـــة ولكنها تسمح بقيم معقولة للقيمة الكلية للايقين بدرجة الثقة المصاحبة.

يبدو موضوع اللايقين في نتائج القياس موضوعا معقدا ولهذا ينهج دليل الأيزو نهجا منطقيا في تناول الموضوع يستحق التلخيص

(أ) أن هناك كمية مدخلة (مدخل) Input Quantity لعملية القياس مثل : قيمة اللايقين في شهادة معايرة الجهاز المستخدم في القياس أو تأثير درجة حرارة البيئة المحيطة أو تكرارية عملية القياس أو تراكيب من تلك العوامل.ويتم الرمز لهذه الكمية المدخلة بالرمز x ولما كانت – عادة – هناك أكثر من كمية مدخلة فنرمز للكمية بالرمز x_I .

(ب) اللايقين المعياري للكمية المدخلة x_I يمثل بالرمز (x_I) حيث يعرف اللايقين المعياري بأنه انحراف معياري واحد One Standard Deviationيحسب مقداره بقسمة قيمة اللايقين في الكمية المدخلة على معامل (Divisor) تتوقف قيمته على توزيع احتمالي مفترض (توزيع طبيعي / توزيع مستطيل / توزيع مثلث). ويمكن حصر قيم المعامل لأنواع التوزيع الممكن افتراضها وفقا لطبيعة عملية القياس في التالي:

التوزيع الطبيعي	**1**
التوزيع الطبيعي (k = 2)	**2**
توزيع مستطيل	**√3**

توزيع مثلث $\sqrt{6}$

توزيع على شكل حرف U $\sqrt{2}$

(ج) يرمز للكمية المخرجة (الخرج / القيمة التقديرية للكمية المقاسة) لعملية القياس بالرمز y

(د) معامل الحساسية c_I :

معامل تحويل من وحدة إلى أخرى. عندما تكون وحدات الكمية المدخلة على عملية القياس غير وحدات الكمية المخرجة:

مثال: أحد العناصر المؤثرة على عملية قياس مثل معايرة قوالب القياس (وحدة أطوال/ ملليمتر) هو تأثير درجة الحرارة (درجة مئوية).في مثل هذه الأحوال يلزم إدخال معامل حساسية بحيث يمكن الربط بين الكمية المدخلة x_I والكمية المخرجة y

(و) يتم تجميع الكميات المخرجة لكل كمية مدخلة x_I في شكل لا يقين معياري (انحراف معياري واحد) يتم تجميعهم بأخذ الجذر التربيعي لمجموع مربعات هذه القيم للايقين المعياري. ويعطي هذا الجذر التربيعي القيمة الكلية للايقين المعياري

(ز) Uc (y) Combined standard uncertainty

يرمز لها بالرمز Expanded Uncert. قيمة موسعة للايقين

U = k uc(y)

يتم استخدام المعامل العددي k لزيادة قيمة اللايقين المعياري uc(y) المعبر عنها في صورة انحراف معياري واحد حيث لا يعطى درجة كافية من الثقة لغالبية أغراض القياس في أن "القيمة الحقيقية" تقع داخل القيم المحددة للايقين.

وفي أغلب الحالات والأغراض يستعمل k=2 لنحصل على نسبة ثقة حوالي 95 %

(ح) وعندئذ تكتب نتيجة القياس عادة في الشكل

y +/- U .

لا يكتمل ه ذا التعبير عن نتائج القياس بدون تحديد قيمة المعامل العددي المستخدم في تحديد القيمة الموسعة للايقين U وكذلك بيان نسبة الثقة.

نموذج جدول موازنة اللايقين

مصدر اللايقين	القيمة x_I $\pm$	التوزيع الاحتمالي	معامل القسمة	معامل الحساسية c_i	$u(x_I)$ $\pm$	v_i أو v_{eff}
القيمة الكلية للايقين المعياري $u_c(y)$						
القيمة الموسعة للايقين $U = k\,u_c(y)$		k=2				

تحليل نتائج القياس

الهـدف:

تهدف عمليات تحليل ومقارنات نتائج القياس إلى:

- **التعرف على مدى دقة القياس في كل معمل من المعامل التي يشملها النظام القومي للقياس خاصة تلك التي تطلب اعتماد معاملها وتقييمها بين الحين والآخر**
- **تعيين قيمة ثابت فيزيائي من نتائج مجموعة من المعامل**
- **مقارنة القيم المتوسطة لمجموعة من التجارب بقيمة عيارية أخرى**
- **الاعتراف المنهجي بكفاءة المعمل في إجراء اختبار / معايرة في نشاط معين .. في مدى قياس محدد . بدرجة دقة معروفة . بمستوى ثقة معلن طبقا للمواصفات الدولية . يظل هو الهدف البارز.**

الطـــرق:

أكثر الطرق شيوعا واستخداما في علم المترولوجيا للمقارنة بين النتائج الواردة من معامل مختلفة وطرق مختلفة لنفس المقيس:

- **الطريقة الأولى (ANOVA)**
- **الطريقة الثانية (اختبار فيشر)**
- **الطريقة الثالثة (اختبار الكفاءة)**
- **الطريقة الرابعة (منهجية الاستبعاد)**
- **الطريقة الخامسة (X-Bar Chart)**
- **الطريقة السادسة (مخططات التحكم)**
- **الطريقة السابعة (المقارنة المباشرة للنتائج)**

الطريقة الأولى ANOVA

- إحدى الطرق الإحصائية التي تهدف إلى مقارنة كل من النتيجة (ا لمقاسة) و النتيجة (العيارية) والحكم عليهما هل هما (متوافقان معا .. أم غير متوافقين معا) بمعنى آخر إثبات مدى تشابه النتيجتين من عدمه.
- ضرورة أن تكون جميع النتائج المسجلة بالمعمل في نفس الظروف البيئية والمعملية و التجهيزية قدر الإمكان تجنبا لوجود مصادر الخطأ الرتيب.

الطريقة الثانية – إختبار فيشر F Test

- تهدف الطريقة بشكل أساسي إلى مقارنة طريقتين للقياس ببعضهما . الأولى الطريقة تحت التحقق و التقييم والثانية التي أجريت بمعمل عياري مرجعي لتحديد قيمة نفس المقيس.
- تجيب هذه الطريقة على السؤال:. هل الطريقتان متماثلتان ولهما نفس الدقة؟

الطريقة الثالثة – إختبار الكفاءة

إجراء اختبار الكفاءة للمعامل لتحديد مدى إمكانية اعتماده في قيمة محددة و مقاسة

- تفيد هذه الطريقة المعامل التي ترغب في اعتمادها دوليا عند قيمة مقاسة معينة أو المعمل الذي قد تم اعتماده بالفعل مسبقا لكن يراد إجراء متابعة له للتأكد من استمرارية تحقيقه لمبدأ الاعتماد.
- لاتتطلب الطريقة عمليات إحصائية معقدة أو رسومات بيانية وخلافه إنما تتطلب فقط :

1. معرفة القيمة المقاسة في كل من المعمل الذي يطلب الاعتماد و المعمل العياري المرجعي
2. معرفة قيمة اللايقين المحسوبة في كل من المعملين.
3. استخدام معادلة رياضية بسيطة يتم بعدها تقرير ما إذا كان يمكن اعتماد هذا المعمل في نقطة القياس هذه أم لا !! كما يمكن بعدها الحكم على نجاح اختبار الكفاءة للقيمة المقاسة من عدمه

خطوات إجراء اختبار الكفاءة

1 - يتم تحديد كل من مقدار القيمة المقاسة Rv و اللايقين في قياسها $\pm U_{RV}$ بوحدات الـ ppm

2 - يقوم المعمل المطلوب عمل اختبار الكفاءة له بإجراء القياس عند نفس القيم المحددة سلفا بالبروتوكول حيث يتم تعيين مقدار القيمة المقاسة L_V و قيمة اللايقين في قياسها $\pm U_{Lv}$ بوحدات الـ ppm أيضا

3 - يتم التقييم لكل قيمة مقاسة بحساب ما يعرف بـ En Ratio عند هذه القيمة من العلاقة التالية :

$$En = L_V - Rv \; / \sqrt{U_{Lv}^2 + U_{RV}^2}$$

4 - - يجب أن تكون قيمة En المحسوبة من المعادلة أقل من الواحد الصحيح حتى يمكن اعتماد المعمل عند هذه القيمة .. فإذا زادت قيمة En عن الواحد الصحيح فسوف يلزم استبعاد هذه القيمة المقاسة من جدول اعتماد المعمل

الطريقة الرابعة - (منهجية الاستبعاد)

تهدف هذه الطريقة إلى استبعاد القراءة الشاذة والمتطرفة أو تلك شديدة التباعد عن باقي القراءات المأخوذة لنفس المقيس في نفس الظروف ..

- **عند تسجيل عدد كبير من النتائج عند تكرار التجربة لمقيس واحد في نفس الظروف فقد تظهر نتيجة أو أكثر من نتيجة شديدة التباعد عن باقي النتائج**
- **يتم هذا الاستبعاد بعد إجراء عملية إحصائية معينة يتم بعدها اتخاذ القرار المناسب تجاه هذه النتيجة.**
- **خطوات الطريقة ..**

1 - يتم تسجيل عدد n من النتائج على المقيس الواحد وفي نفس ظروف التجربة بحيث لا يكون هناك شك في إحدى النتائج المأخوذة

قد تكون أصغر النتائج هي شديدة التباعد عن باقي المجموعة و مشكوك فيها ..هنا نرتب النتائج ترتيبا تصاعديا من الأصغر إلى الأكبر

(X1 < X2 < X3 <……. < Xn)

2 - أو قد تكون أكبر النتائج هي شديدة التباعد عن باقي المجموعة ومشكوك فيها .. هنا نرتب النتائج ترتيبا تنازليا من الأكبر إلى الأصغر

(X1 > X2 > X3 > ……. > Xn)

3 - هب أننا بصدد الاحتمال الأول كما في الخطوة 2 ، وأن عدد النتائج المأخوذة يقع بين 3 الى 7 قراءات ..نحسب قيمة المدى بين أصغر قيمة و القيمة التالية لها و لتكن X2 – X1 ثم نحسب المدى بين أصغر قيمة و أكبر قيمة (أي خلال المدى بالكامل) و لتكن Xn – X1

4 - نحسب النسبة بين المقدارين السابقين (r10) كما يلي:

$$r10 = (X2 - X1) / (Xn - X1)$$

5 - نقارن الآن بين قيمة r10 المحسوبة من العلاقة السابقة وبين قيمتها من الجدول وعند درجة معنوية 5% (مستوى ثقة 95%) أو عند درجة معنوية 1 % (مستوى ثقة 99%) فإذا كانت القيمة المحسوبة من العلاقة أكبر من القيمة الموجودة بالجدول فإنه من الأفضل استبعاد هذه النتيجة

g	عدد التجارب	p= 5%	p= 1%
$r_{10} = \frac{x_2 - x_1}{x_n - x_i}$	3	0.941	0.988
	4	0.765	0.889
	5	0.642	0.780
	6	0.560	0.698
	7	0.507	0.637
$r_{11} = \frac{x_2 - x_1}{x_{n-1} - x_i}$	8	0.554	0.683
	9	0.512	0.635
	10	0.477	0.597
$r_{21} = \frac{x_2 - x_1}{x_{n-1} - x_i}$	11	0.576	0.679
	12	0.546	0.642
	13	0.521	0.615
$r_{22} = \frac{x_3 - x_1}{x_{n-2} - x_i}$	14	0.546	0.641
	15	0.525	0.616
	16	0.507	0.595
	17	0.490	0.577
	18	0.475	0.561
	19	0.462	0.547
	20	0.450	0.535
	21	0.440	0.524
	22	0.430	0.514
	23	0.421	0.505
	24	0.413	0.497
	25	0.406	0.489

- **ملاحظة هامة ..**

في حالة زيادة عدد التجارب عن 7 فإنه من المناسب استخدام علاقات أخرى تقابل هذه الزيادة في عدد النتائج

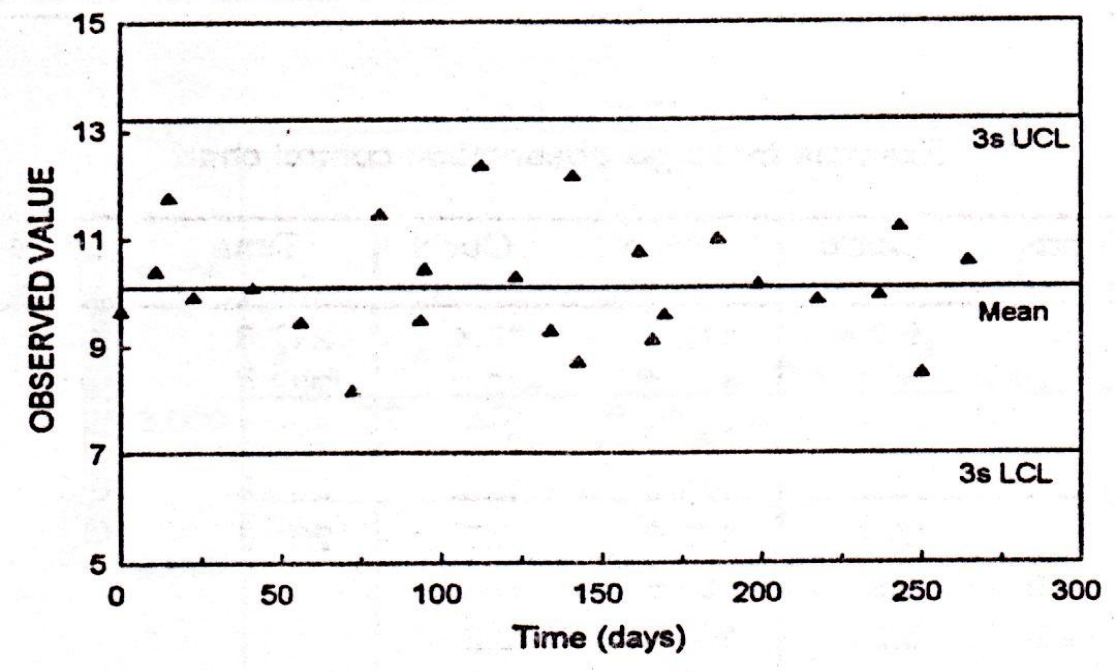
الطريقة الخامسة - X – Bar Chart

أسلوب بياني إحصائي للحكم على أداء النتائج المأخوذة بأنه تحت السيطرة و التحكم

- **تهدف إلى الحكم على عملية قياس معينة من حيث كونها تحت التحكم والسيطرة.**
- **اختبار ما يعرف بـ (مدى الاستقرارية) لنتيجة قياس معين.**

من أمثلة تطبيق هذه الطريقة معايرة جهاز مرجعي أو قيمة عيارية تتم دوريا خلال مدى عريض من الزمن قد يصل إلى عام كامل. كذلك يمكن تطبيقها على نتيجة متوسطة مأخوذة من عدد كبير من النتائج بحيث يتكرر أخذ هذه القيمة المتوسطة مرات ومرات خلال فترة زمنية طويلة

يعتد بها كعنصر أساسي من عناصر طرق توكيد



الطريقة السادســـة – مخططات التحكم

Control Charts:

طريقة إحصائية بيانية لضبط وتوكيد صحة القياس.

أسلوب تخطيطي للحكم على أداء عمليات القياس إذا كان في حالة التحكم والسيطرة الإحصائية من عدمه.

تفيد في حالات مقارنة التغيرات الحادثة في قيمة عيارية بحدود التحكم المسموح بها لهذه القيمة.

الدور الرئيسي لهذه المخططات هو حساب تلك الحدود التي يجب أن تقع خلالها قيمة قياسية معينة حتى نحكم عليها أنها في حالة الاستقرار الإحصائي و أن التغيرات التي يمكن أن تحدث بها في نطاق الموافقة والقبول.

- **الطريقة السابعة – المقارنة المباشرة للنتائج**

تهدف الطريقة إلىإجراء مقارنة سريعة وبسيطة لنتائج المعامل المشاركة في حلقة قياس مغلقة حول قيمة عيارية معينة بحيث تشمل هذه المقارنة السريعة مقارنة كل من القيم المتوسطة للنتائج وكذلك اللايقين المصاحب لهذه القيمة المتوسطة وذلك من خلال مخطط بياني بسيط.

هناك حالاتين:

1- الحالة الأولى .. عدم وجود معمل عياري محوري تستند إليه نتائج المعامل المشاركة:

يجدر أن تكون المعامل المشاركة معامل عيارية مرجعية متقاربة في مستوى الدقة وكذلك في مستوى الإمكانيات من جهة أنظمة و أجهزة القياس المستخدمة أو العنصر البشري المؤهل جيدا.

يتم اختيار جهاز عياري أو كمية عيارية معينة يمكن تداولها بين المعامل المشاركة بحيث تصبح عنصرا رحالا يتم قياسه من خلال المعامل المشاركة كل على حده من خلال بروتوكول معين يتم الاتفاق على بنوده من خلال المعامل المشاركة ذاتها.

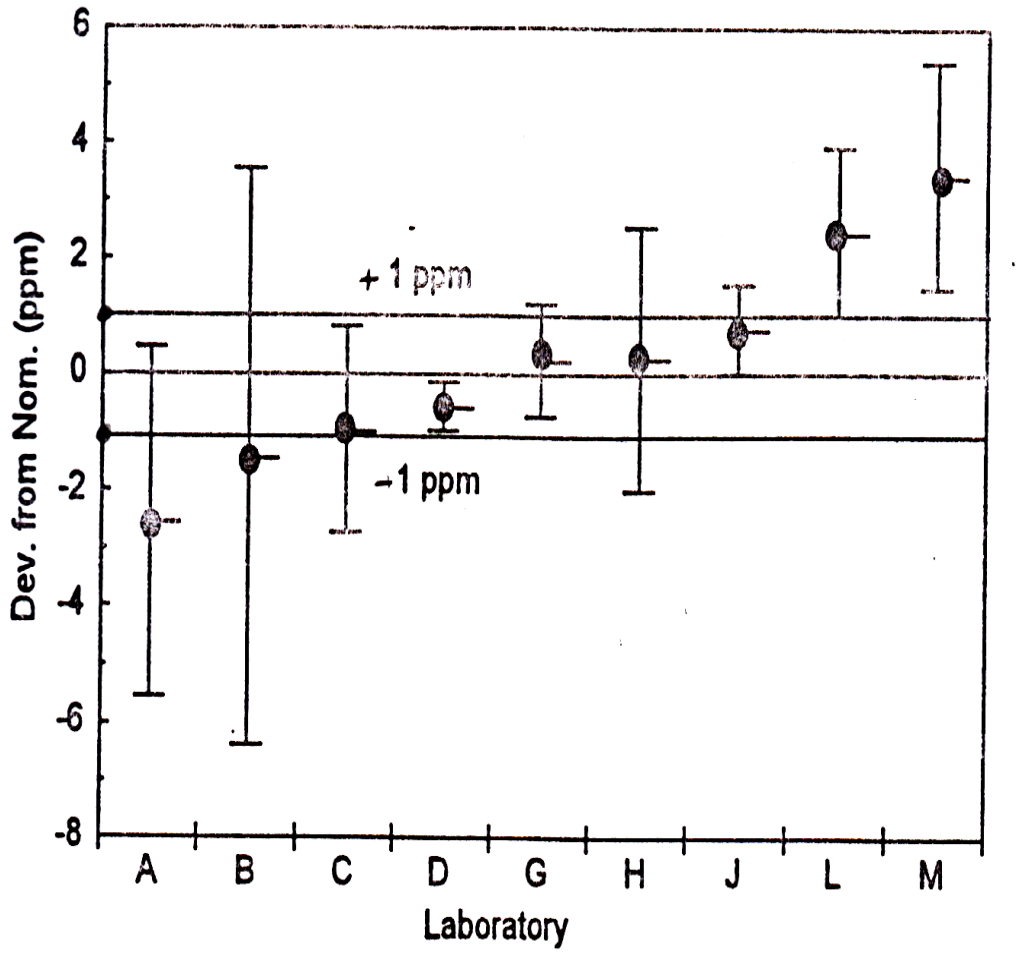
يتم تجميع النتائج التي سجلت في هذه المعامل بواسطة محلل النتائج وكذلك يتم إمداده بمقدار اللايقين المصاحب لهذه النتائج.

يتم حساب المتوسط الحسابي الكلي للنتائج المجمعة من كل المعامل المشاركة حيث يمثل هذا المتوسط الحسابي القيمة العيارية الصحيحة التي تقارن بها قراءات المعامل المشاركة.

يتم حساب فروق (انحرافات) نتائج المعامل المشاركة عن قيمة المتوسط الحسابي الكلي المحسوب = (المتوسط الحسابي الكلي – قراءة المعمل)

يتم حساب ما يعرف بخط أو شريط الخطأ (Error Bar) لكل معمل وهو عبارة عن قيمة الانحراف في نتيجة المعمل مضاف إليه (و مطروحا منه) مقدار اللايقين المصاحب لهذه النتيجة أي (Δ Eobs. $\pm$ U)

المخطـط البيـــاني



ـ الحالة الثانية .. وجود معمل عياري محوري تستند إليه المعامل المشاركة:

لا يختلف الحال هنا كثيرا عن الحالة السابقة إلا في أمرين :

1) طريقة حساب الخط الصفري المحوري الذي ستقارن به بقية النتائج. في هذه الحالة يتم تعيين القيمة العيارية الموضوعة تحت الاختبار بالمعمل العياري المحوري (Pivot Lab.) مرتين إحداهما في بداية حلقة القياس المغلقة و الأخرى في نهاية الحلقة بعد انتهاء القياس بالمعامل الأخرى المشاركة

طريقة حساب حدي المواصفات القياسية الأعلى والأدنى المطلوب انحصار جميع القياسات بينهما

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الكـيمـياء غير العضويه المتقدمه

الملحقات

Advanced Inorganic Chemistry

Annexes

Assistant Prof. Mona Khorshed

Central Laboratory of Residue Analysis of Pesticides and Heavy Metals in Food.

July 2008

Deutsche Gesellschaft für Technische Zusammenarbeit - GTZ

Water and Wastewater Management Programme

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Annex 1

الملحق الأول

ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Method 3005 is an acid digestion procedure used to prepare surface and ground water samples for analysis by flame atomic absorption spectroscopy (FLAA) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3005 may be analyzed by AAS or ICP for the following metals:

Aluminum	Magnesium
Antimony**	Manganese
Arsenic*	Molybdenum
Barium	Nickel
Beryllium	Potassium
Cadmium	Selenium*
Calcium	Silver
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

* ICP only
**May be analyzed by ICP, FLAA, or GFAA

1.2 When analyzing for total dissolved metals filter the sample, at the time of collection, prior to acidification with nitric acid.

2.0 SUMMARY OF METHOD

2.1 Total recoverable metals - The entire sample is acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is filtered and diluted to volume, and is then ready for analysis.

2.2 Dissolved metals - The sample is filtered through a 0.45-µm filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid. Samples for dissolved metals do not need to be digested as long as the acid concentrations have been adjusted to the same concentration as in the standards.

3.0 INTERFERENCES

3.1 The analyst should be cautioned that this digestion procedure may not be sufficiently vigorous to destroy some metal complexes.

Precipitation will cause a lowering of the silver concentration and therefore an inaccurate analysis.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers of assorted sizes or equivalent.

4.2 Watch glasses or equivalent.

4.3 Qualitative filter paper and filter funnels.

4.4 Graduated cylinder or equivalent.

4.5 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Both plastic and glass containers are suitable.

6.3 Sampling

6.3.1 Total recoverable metals - All samples must be acidified at the time of collection with HNO_3 (5 mL/L).

6.3.2 Dissolved metals - All samples must be filtered through a 0.45-µm filter and then acidified at the time of collection with HNO_3 (5 mL/L).

7.0 PROCEDURE

7.1 Transfer a 100-mL aliquot of well-mixed sample to a beaker.

7.2 For metals that are to be analyzed, add 2 mL of concentrated HNO_3 and 5 mL of concentrated HCl. The sample is covered with a ribbed watch glass or other suitable covers and heated on a steam bath, hot plate or other heating source at 90 to 95°C until the volume has been reduced to 15-20 mL.

CAUTION: Do not boil. Antimony is easily lost by volatilization from hydrochloric acid media.

7.3 Remove the beaker and allow to cool. Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer; this additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3.

7.4 Adjust the final volume to 100 mL with reagent water.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. Replicate samples will be used to determine precision. The sample load will dictate the frequency, but 5% is recommended. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch. Refer to Chapter One for the proper protocol when analyzing spikes.

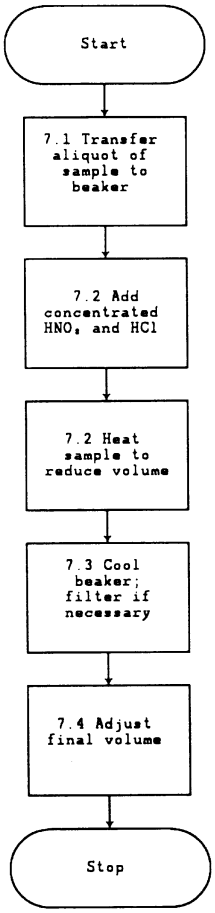
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.


Start
7.1 Transfer aliquot of sample to beaker
7.2 Add concentrated HNO3 and HCl
7.2 Heat sample to reduce volume
7.3 Cool beaker; filter if necessary
7.4 Adjust final volume
Stop

METHOD 3015

MICROWAVE ASSISTED ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis, by flame atomic absorption spectroscopy (FLAA), graphite furnace absorption spectroscopy (GFAA), inductively coupled argon plasma spectroscopy (ICP), or inductively coupled argon plasma mass spectrometry (ICP-MS). The procedure is a hot acid leach for determining available metals. Due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system and refer to the SW-846 "DISCLAIMER" when conducting analyses using Method 3015.

1.2 Samples prepared by Method 3015 using nitric acid digestion may be analyzed by FLAA, GFAA, ICP-AES, or ICP-MS for the following:

Aluminum	Lead
Antimony	Magnesium
Arsenic*	Manganese
Barium	Molybdenum
Beryllium	Nickel
Cadmium	Potassium
Calcium	Selenium*
Chromium	Silver
Cobalt	Sodium
Copper	Thallium
Iron	Vanadium
	Zinc

*Cannot be analyzed by FLAA

2.0 SUMMARY OF METHOD

2.1 A representative 45 mL aqueous sample is digested in 5 mL of concentrated nitric acid in a fluorocarbon (PFA or TFM) digestion vessel for 20 minutes using microwave heating. After the digestion process, the sample is cooled, and then filtered, centrifuged, or allowed to settle in a clean sample bottle prior to analysis.

3.0 INTERFERENCES

3.1 Many samples that contain organics, such as TCLP extracts, will result in higher vessel pressures which have the potential to cause venting of the vessels. Venting can result in either loss of analytes and/or sample, which

must be avoided. A smaller sample size can be used but the final water volume prior to nitric acid addition must remain at 45 mL. This is required to retain the heat characteristics of the calibration procedure. Limits of quantitation will change with sample quantity (dilution) as with instrumentation."

4.0 APPARATUS AND MATERIALS

4.1 Microwave apparatus requirements

4.1.1 The microwave unit provides programmable power with a minimum of 574 W, which can be programmed to within ± 10 W of the required power. Typical units provide a nominal 600 W to 1200 W of power. Temperature monitoring and control of the microwave unit are desirable.

4.1.2 The microwave unit cavity is corrosion resistant and well ventilated.

4.1.3 All electronics are protected against corrosion for safe operation.

4.1.4 The system requires fluorocarbon (PFA or TFM) digestion vessels (120 mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psig) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psig).

4.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.

CAUTION: Those laboratories now using or contemplating the use of kitchen type microwave ovens for this method should be aware of several significant safety issues. First, when an acid such as nitric is used to assist sample digestion in microwave units in open vessels, or sealed vessels equipped with venting features, there is the potential for the acid gases released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a unit with corrosion resistant safety devices prevents this from occurring.

CAUTION: The second safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained. However, many digestion vessels constructed from certain fluorocarbons may crack, burst, or explode in the oven under certain pressures. Only unlined fluorocarbon (PFA or TFM) containers with pressure relief mechanisms or containers with fluorocarbon (PFA or TFM) liners and pressure relief mechanisms are considered acceptable at present.

Users are therefore advised not to use kitchen type microwave ovens or to use sealed containers without pressure relief valves for microwave acid digestions by this method. Use of laboratory grade microwave equipment is required to prevent safety hazards. For further information consult reference 1.

CAUTION: In addition, there are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. These specific suggestions are beyond the scope of this method and require the analyst to consult the specific equipment manual, manufacturer and literature for proper and safe operation of the microwave equipment and vessels.

4.2 Volumetric graduated cylinder, 50 or 100 mL capacity or equivalent.

4.3 Filter paper, qualitative or equivalent.

4.4 Analytical balance, 300 g capacity, minimum accuracy ± 0.01 g.

4.5 Filter funnel, glass or disposable polypropylene.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified (Ref. 2).

5.3 Concentrated nitric acid, HNO_3. Acid should be analyzed to determine levels of impurities. If the method blank is less than the MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic containers are preferable. See Chapter Three, Step 3.1.3 of this manual, for further information.

6.3 Aqueous waste waters must be acidified to a pH of < 2 with HNO_3.

7.0 PROCEDURE

7.1 Calibration of Microwave Equipment

NOTE: If the microwave unit uses temperature feedback control capable of replicating the performance specifications of the method, then the calibration procedure may be omitted.

7.1.1 Measurement of the available power for heating is evaluated so that absolute power in watts may be transferred from one microwave unit to another. For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the unit. The calibration format required for laboratory microwave units depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (7.1.3), otherwise, the analyst must use the multiple point calibration method (7.1.2).

7.1.2 The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured; 100,99,98,97, 95,90,80,70,60,50, and 40% using the procedure described in section 7.1.4. This data is clustered about the customary working power ranges. Nonlinearity has been commonly encountered at the upper end of the calibration. If the unit's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (±10 W), then the entire calibration should be reevaluated.

7.1.3 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using the procedure described in section 7.1.4, and calculate the power setting corresponding to the required power in watts specified in the procedure from the (2-point) line. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ±10 W, use the multiple point calibration in 7.1.2. This point should also be used to periodically verify the integrity of the calibration.

7.1.4 Equilibrate a large volume of water to room temperature (23 ± 2 °C). One kg of reagent water is weighed (1,000.0 g $\pm$ 0.1 g) into a fluorocarbon (PFA or TFM) beaker or a beaker made of some other

material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be 23 ± 2 °C measured to ± 0.05 °C. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the unit's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 30 seconds to ± 0.05 °C. Use a new sample for each additional measurement. If the water is reused both the water and the beaker must have returned to 23 ± 2 °C. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship

$$P = \frac{(K)\ (C_p)\ (m)\ (\Delta T)}{t} \qquad \text{Eq. 1}$$

Where:

P = the apparent power absorbed by the sample in watts (W). (W=joule·sec^{-1})

K = the conversion factor for thermochemical calories·sec^{-1} to watts (=4.184)

C_p = the heat capacity, thermal capacity, or specific heat (cal·g^{-1}·$°C^{-1}$), of water

m = the mass of the water sample in grams (g)

ΔT = the final temperature minus the initial temperature (°C)

t = the time in seconds (s)

Using the experimental conditions of 2 minutes and 1 kg of distilled water (heat capacity at 25 °C is 0.9997 cal·g^{-1}·$°C^{-1}$) the calibration equation simplifies to:

$$P = (\Delta T)\ (34.86)$$

NOTE: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation not vary by more than ±2 V. A constant power supply may be necessary for microwave use if the source of the line voltage is unstable.

Electronic components in most microwave units are matched to the units' function and output. When any part of the high voltage circuit, power source, or control components in the unit have been serviced or replaced, it will be necessary to recheck the units' calibration power. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

7.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high solids (concentrated) samples and low solids (low concentration) samples all digestion vessels should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80°C, but less than boiling) for a minimum of two hours followed with hot (1:1) nitric acid (greater than 80°C, but less than boiling) for a minimum of two hours, rinsed with reagent water, and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware and storage containers should be cleaned by leaching with more dilute acids (approximately 10% V/V) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. In addition, to avoid precipitation of silver, ensure that all HCl has been rinsed from the vessels.

7.3 Sample Digestion

7.3.1 Weigh the fluorocarbon (PFA or TFM) digestion vessel, valve and cap assembly to 0.01 g prior to use.

7.3.2 A 45 mL aliquot of a well shaken sample is measured in a graduated cylinder. This aliquot is poured into the digestion vessel with the number of the vessel recorded on the preparation sheet.

7.3.3 A blank sample of reagent water is treated in the same manner along with spikes and duplicates.

7.3.4 Add 5 mL of concentrated nitric acid to each vessel that will be used. Check to make sure the pressure relief disks are in the caps with the smooth side toward the sample and start the caps a few turns on the vessels. Finish tightening the caps in the capping station which will tighten them to a uniform torque pressure of 12 ft-lbs. (16 N-m) or to the manufacturers recommended specifications. Weigh each capped vessel to the nearest 0.01 g.

CAUTION: Toxic nitrogen oxide fumes may be evolved, therefore all work must be performed in a properly operating ventilation system. The analyst should also be aware of the potential for a vigorous reaction. If a vigorous reaction occurs, allow to cool before capping the vessel.

7.3.5 Evenly distributed the vessels in the carousel according to the manufacturer's recommended specifications. Blanks are treated

as samples for the purpose of balancing the power input. When fewer than the recommended number of samples are digested, the remaining vessels should be filled with 45 mL of reagent water and 5 mL of nitric acid to achieve the full compliment of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity (Ref. 1).

7.3.6 Program the microwave unit according to the manufacturer's recommended specifications and, if used, connect the pressure vessels to the central overflow vessel with PFA-fluorocarbon tubes. The chosen sequence will bring the samples to 160°C ± 4°C in 10 minutes and will permit a slow rise to 165-170 °C during the second 10 minutes (Ref. 3). Start the turntable motor and be sure the vent fan is running on high and the turntable is turning. Start the microwave generator.

7.3.6.1 Newer microwave units are capable of higher power that permit digestion of a larger number of samples per batch. If the analyst wishes to digest more samples at a time, the analyst may use different power settings as long as they result in the same time and temperature conditions defined in 7.3.6. That is, any sequence of power that brings the samples to 160°C ± 4°C in 10 minutes and permits a slow rise to 165-170°C during the second 10 minutes (Ref. 2).

Issues of safety, structural integrity (both temperature and pressure limitations), heat loss, chemical compatibility, microwave absorption of vessel material, and energy transport will be considerations made in choosing alternative vessels. If all of the considerations are met and the appropriate power settings are provided to reproduce the reaction conditions defined in 7.3.6, then these alternative vessels may be used (Ref. 1,3)

7.3.7 At the end of the microwave program, allow the vessels to cool for at least 5 minutes in the unit before removal to avoid possible injury if a vessel vents immediately after microwave heating. The samples may be cooled outside the unit by removing the carousel and allowing the samples to cool on the bench or in a water bath. When the vessels have cooled to room temperature, weigh and record the weight of each vessel assembly. If the weight of the sample plus acid has decreased by more than 10% discard the sample.

7.3.8 Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged, allowed to settle or filtered.

7.3.8.1 Centrifugation: Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.3.8.2 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

7.3.8.3 Filtering: The filtering apparatus must be thoroughly cleaned and prerinsed with dilute (approximately 10% V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned cotainer.

7.3.9 The concentration values obtained from analysis must be corrected for the dilution factor from the acid addition. If the sample will be analyzed by ICP-MS additional dilution will generally be necessary. For example, the sample may be diluted by a factor of 20 with reagent water and the acid strength adjusted back to 10% prior to analysis. The dilutions used should be recorded and the measured concentrations adjusted accordingly (e.g., for a 45 mL sample and 5 mL of acid the correction factor is 1.11).

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One, of this Manual, should be followed.

8.2 For each analytical batch of samples processed, analytical reagent blanks (also field blanks if they were taken) should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.3 Duplicate samples should be processed on a routine basis. A duplicate sample is a real sample brought through the whole sample preparation and analytical process. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Refer to Table 1 for a summary of performance data.

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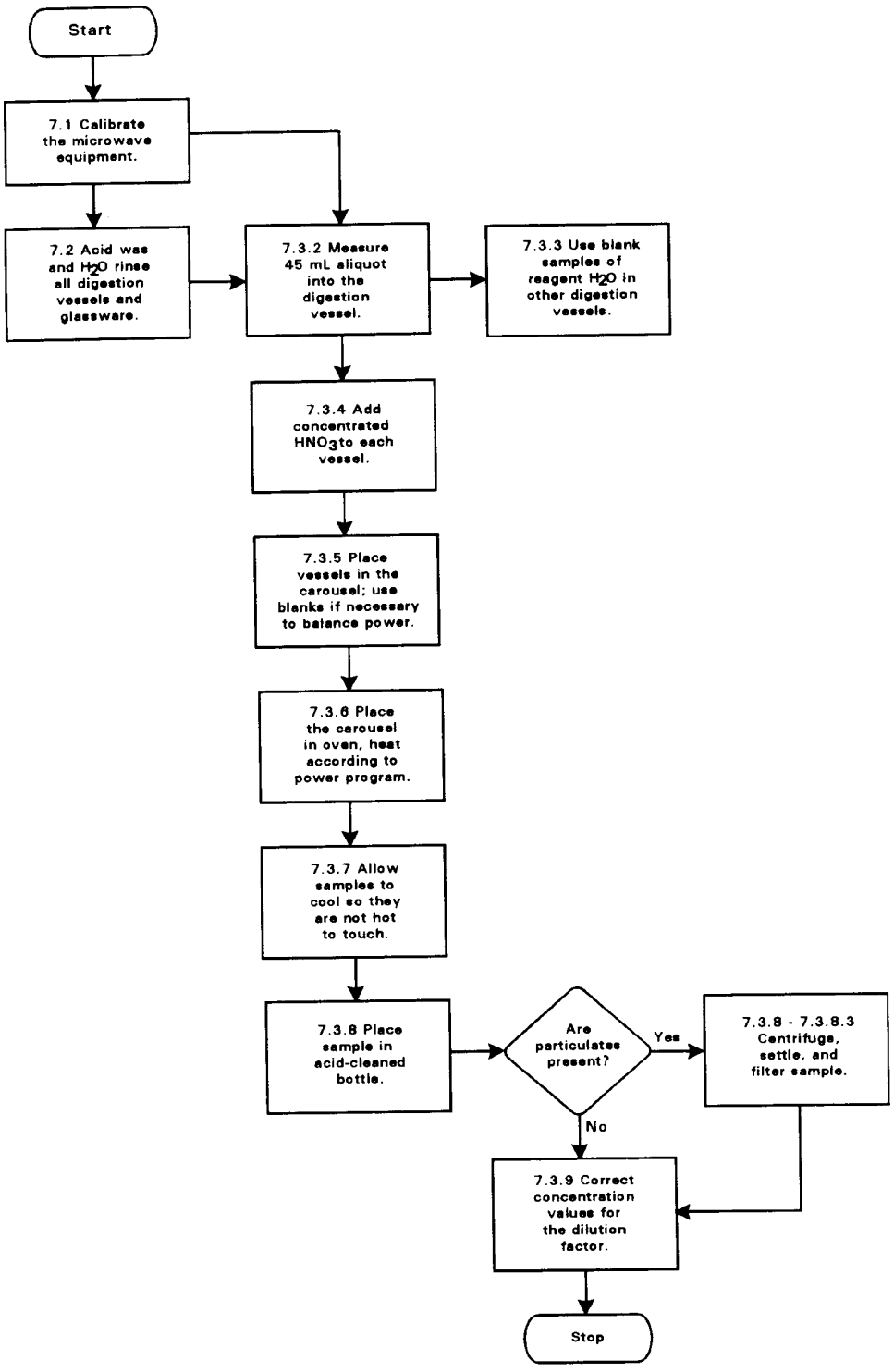
TABLE 1
MICROWAVE DIGESTION METHOD 3015 (Nitric Acid Only)

Elem	Material	Certified Mean	Observed Mean	Std. Dev.	Relative Standard Deviation	Relative Bias
Al	Tm-11	510.0	485.5	26.3	5.4	-4.80%
Al	Tm-12	2687.0	2770.6	88.2	3.2	3.11%
Al	T-107	220.0	213.5	19.3	9.0	-2.95%
Al	T-109	113.0	117.7	30.6	2.6	4.16%
Ba	Tm-11	450.0	441.4	23.4	5.3	-1.90%
Ba	Tm-12	2529.0	2431.4	70.3	2.9	-3.86%
Ba	T-107	192.0	196.6	15.9	8.1	2.44%
Cd	Tm-11	40.8	44.6	2.1	4.7	9.46%
Cd	Tm-12	237.0	242.3	8	3.3	2.25%
Cd	T-107	14.3	12.4	0.9	7.2	-12.94%
Cd	T-109	12.1	10.3	1.7	16.5	-14.55%
Zn	Tm-11	55.4	55.9	2.6	4.6	1.06%
Zn	Tm-12	314.0	316.5	8.9	2.8	0.82%
Zn	T-107	75.8	81.6	3.3	4.0	7.68%
Zn	T-109	74.0	69.9	4.1	5.8	-5.46%
As	T-107	10.8	12.8	0.84	6.5	19.26%
As	T-109	8.15	90.6	11.0	12.2	11.26%
Co	Tm-11	227.0	242.6	14.1	5.8	6.90%
Co	Tm-12	1067.0	1153.3	35.9	3.1	8.09%
K	T-95	4700.0	5080.3	784	15.4	8.09%
K	T-109	2330.0	2601.5	383.4	14.7	11.65%
Ni	Tm-11	264.0	284.3	16.5	5.8	7.71%
Ni	Tm-12	1234.0	1293.0	39.4	3.0	4.79%
Ni	T-109	57.0	60.8	3.09	5.0	6.72%
Pb	Tm-11	275.0	275.9	32.2	11.7	0.36%
Pb	Tm-12	1326.0	1359.0	35.0	2.6	2.49%
Pb	T-107	26.0	30.0	0.2	0.66	15.65%
Pb	T-109	34.9	39.3	1.2	3.0	12.69%
Sb	WP980-1	16.9	18.3	0.47	2.6	8.27%
Sb	WP980-2	101.5	108.9	34.4	31.6	7.33%
Se	T-95	60.1	65.9	2.6	3.94	9.77%
Se	T-107	11.0	13.0	0.9	6.9	19.00%
Tl	WP980-1	50.0	55.1	2	3.6	10.26%
Tl	WP980-2	6.3	7.0	0.52	7.4	11.66%
V	Tm-11	491.0	532.6	26.1	4.9	8.48%
V	Tm-12	2319.0	2412.8	60.6	2.5	4.05%
Be	T-107	11.0	11.3	0.53	4.7	3.00%
Be	T-109	22.1	25.6	0.91	3.6	15.97%
Ca	T-107	11700.0	12364.0	783.6	6.3	5.68%
Ca	T-109	35400.0	38885.0	999	2.6	9.84%

TABLE 1 (continued)

Elem	Material	Certified Mean	Observed Mean	Std. Dev.	Relative Standard Deviation	Relative Bias
Mg	T-95	32800.0	35002.0	1900	5.4	6.71%
Mg	T-107	2100.0	2246.7	110.5	4.9	6.99%
Mg	T-109	9310.0	10221.7	218.6	2.1	9.79%
Na	T-95	190000.0	218130.0	10700	4.9	14.81%
Na	T-107	20700.0	22528.0	1060	4.7	8.83%
Na	T-109	12000.0	13799.5	516.2	3.7	15.00%
Cr	Tm-11	52.1	64.3	4.1	6.4	23.51%
Cr	Tm-12	299.0	346.0	9.8	2.8	15.74%
Cr	T-107	13.0	22.3	1.5	6.7	71.77%
Cr	T-109	18.7	32.6	6.4	19.6	74.71%
Cu	Tm-11	46.3	76.5	4.4	5.7	65.36%
Cu	Tm-12	288.0	324.0	8.9	2.7	12.52%
Cu	T-107	30.0	42.3	4.0	9.4	41.17%
Cu	T-109	21.4	54.0	3.6	6.7	152.38%
Fe	Tm-11	249.0	289.3	16.4	5.7	16.18%
Fe	Tm-12	1089.0	1182.5	43.5	3.7	8.59%
Fe	T-107	52.0	63.8	8.7	13.6	22.69%
Fe	T-109	106.0	134.0	6.6	4.9	26.50%
Mn	Tm-11	46.0	60.9	3.2	5.2	32.48%
Mn	Tm-12	263.0	304.4	9.1	3.0	15.77%
Mn	T-107	45.0	52.6	3.1	5.9	17.09%
Mn	T-109	34.0	46.6	3.0	6.4	37.18%
Ag	WS378-1	46.0	19.4	5.6	2.9	-57.83%


Start
7.1 Calibrate the microwave equipment.
7.2 Acid was and H_2O rinse all digestion vessels and glassware.
7.3.2 Measure 45 mL aliquot into the digestion vessel.
7.3.3 Use blank samples of reagent H_2O in other digestion vessels.
7.3.4 Add concentrated HNO_3 to each vessel.
7.3.5 Place vessels in the carousel; use blanks if necessary to balance power.
7.3.6 Place the carousel in oven, heat according to power program.
7.3.7 Allow samples to cool so they are not hot to touch.
7.3.8 Place sample in acid-cleaned bottle.
Are particulates present?
Yes
7.3.8 - 7.3.8.3 Centrifuge, settle, and filter sample.
No
7.3.9 Correct concentration values for the dilution factor.
Stop

METHOD 3051

MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the microwave assisted acid digestion of sludges, sediments, soils, and oils for the following elements:

Aluminum	Cadmium	Iron	Molybdenum	Sodium
Antimony	Calcium	Lead	Nickel	Strontium
Arsenic	Chromium	Magnesium	Potassium	Thallium
Boron	Cobalt	Manganese	Selenium	Vanadium
Barium	Copper	Mercury	Silver	Zinc
Beryllium				

1.2 This method is provided as an alternative to Method 3050. It is intended to provide a rapid multielement acid leach digestion prior to analysis so that decisions can be made about site cleanup levels, the need for TCLP testing of a waste and whether a BDAT process is providing acceptable performance. If a decomposition including hydrochloric acid is required for certain elements, it is recommended that Method 3050A be used. Digests produced by the method are suitable for analysis by flame atomic absorption (FLAA), graphite furnace atomic absorption (GFAA), inductively coupled plasma emission spectroscopy (ICP-ES) and inductively coupled plasma mass spectrometry (ICP-MS). Due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system and refer to the SW-846 "DISCLAIMER" when conducting analyses using Method 3051.

2.0 SUMMARY OF METHOD

2.1 A representative sample of up to 0.5 g is digested in 10 mL of concentrated nitric acid for 10 min using microwave heating with a suitable laboratory microwave unit. The sample and acid are placed in a fluorocarbon (PFA or TFM) microwave vessel. The vessel is capped and heated in the microwave unit. After cooling, the vessel contents are filtered, centrifuged, or allowed to settle and then diluted to volume and analyzed by the appropriate SW-846 method (Ref. 1).

3.0 INTERFERENCES

3.1 Very reactive or volatile materials that may create high pressures when heated may cause venting of the vessels with potential loss of sample and analytes. The complete decomposition of either carbonates, or carbon based samples, may cause enough pressure to vent the vessel if the sample size is greater than 0.25 g when used in the 120 mL vessels with a pressure relief device that has an upper limit of 7.5 ± 0.7 atm (110 ± 10 psi).

4.0 APPARATUS AND MATERIALS

4.1 Microwave apparatus requirements.

4.1.1 The microwave unit provides programmable power with a minimum of 574 W, which can be programmed to within ± 10 W of the required power. Typical units provide a nominal 600 W to 1200 W of power. Pressure, or especially temperature, monitoring and control of the microwave unit are desirable.

4.1.2 The microwave unit cavity is corrosion resistant and well ventilated.

4.1.3 All electronics are protected against corrosion for safe operation.

4.1.4 The system requires fluorocarbon (PFA or TFM) digestion vessels (120 mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psi).

4.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.

> CAUTION: Those laboratories now using or contemplating the use of kitchen type microwave ovens for this method should be aware of several signifant safety issues. First, when an acid such as nitric is used to assist sample digestion in microwave units in open vessels, or sealed vesselsequippedres, there is the potential for the acid gases released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a unit with corrosion resistant safety devices prevents this from occurring.
>
> CAUTION: The second safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained. However, many digestion vessels constructed from certain fluorocarbons may crack, burst, or explode in the unit under certain pressures. Only unlined fluorocarbon (PFA or TFM) containers with pressure relief mecahnisms or containers with PFA-fluorocarbon liners and pressure relief mechanisms are considered acceptable at present.

Users are therefore advised not to use kitchen type microwave ovens or to use sealed containers without pressure relief valves for microwave acid digestions by this method. Use of laboratory-grade microwave equipment is required to prevent safety hazards. For further details consult reference 2.

CAUTION: There are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. These specific suggestions are beyond the scope of this method and require the analyst to consult the specific equipment manual, manufacturer and literature for proper and safe operation of the microwave equipment and vessels.

4.2 Volumetric graduated cylinder, 50 or 100 mL capacity or equivalent.

4.3 Filter paper, qualitative or equivalent.

4.4 Filter funnel, glass or disposable polypropylene.

4.5 Analytical balance, 300 g capacity, and minimum ± 0.01 g.

5.0 REAGENTS

5.1 All acids should be sub-boiling distilled where possible to minimize the blank levels due to metallic contamination. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.1.1 Concentrated nitric acid, HNO_3. Acid should be analyzed to determine levels of impurity. If the method blank is less than the MDL, the acid can be used.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified (Ref. 3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids and water. Plastic and glass containers are both suitable. See Chapter Three, sec. 3.1.3 of this manual, for further information.

6.3 Samples must be refrigerated upon receipt and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration of Microwave Equipment

NOTE: If the microwave unit uses temperature feedback control capable of replicating the performance specifications of the method, then the calibration procedure may be omitted.

7.1.1 Measurement of the available power for heating is evaluated so that absolute power in watts may be transferred from one microwave unit to another. For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the unit. The calibration format required for laboratory microwave units depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (7.1.3), otherwise, the analyst must use the multiple point calibration method (7.1.2).

7.1.2 The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured; 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% using the procedure described in section

7.1.4. This data is clustered about the customary working power ranges. Nonlinearity has been commonly encountered at the upper end of the calibration. If the unit's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (±10 W), then the entire calibration should be reevaluated.

7.1.3 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using athe procedure described in section 7.1.4. From the 2-point line calculate the power setting corresponding to the required power in watts specified in the procedure. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ±10 W, use the multiple point calibration in 7.1.2. This point should also be used to periodically verify the integrity of the calibration.

7.1.4 Equilibrate a large volume of water to room temperature (23 ± 2°C). One kg of reagent water is weighed (1,000.0 g $\pm$ 0.1 g) into a

fluorocarbon beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be 23 ± 2°C measured to ± 0.05°C. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the unit's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 30 seconds to ± 0.05°C. Use a new sample for each additional measurement. If the water is reused both the water and the beaker must have returned to 23 ± 2°C. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship:

Eq. 1
$$P = \frac{(K)\ (C_p)\ (m)\ (\Delta T)}{t}$$

Where:

P = the apparent power absorbed by the sample in watts (W) (W=joule·sec^{-1})

K = the conversion factor for thermochemical calories·sec^{-1} to watts (=4.184)

C_p = the heat capacity, thermal capacity, or specific heat (cal·g^{-1}·$°C^{-1}$) of water

m = the mass of the water sample in grams (g)

ΔT = the final temperature minus the initial temperature (°C)

t = the time in seconds (s)

Using the experimental conditions of 2 minutes and 1 kg of distilled water (heat capacity at 25 °C is 0.9997 cal·g^{-1}·$°C^{-1}$) the calibration equation simplifies to:

Eq. 2
$$P = (\Delta T)\ (34.86)$$

> NOTE: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation should not vary by more than ±2 V. A constant power supply may be necessary for microwave use if the source of the line voltage is unstable.

Electronic components in most microwave units are matched to the units' function and output. When any part of the high voltage circuit, power source, or control components in the unit have been serviced or replaced, it will be necessary to recheck the units' calibration. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

7.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high concentration samples and low concentration samples, all digestion vessels should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80°C, but less than boiling) for a minimum of two hours followed with hot (1:1) nitric acid (greater than 80°C, but less than boiling) for a minimum of two hours and rinsed with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware and storage containers should be cleaned by leaching with more dilute acids (approximately 10% V/V) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. To avoid precipitation of silver, ensure that all HCl has been rinsed from the vessels.

7.3 Sample Digestion

7.3.1 Weigh the fluorocarbon (PFA or TFM) digestion vessel, valve and capassembly to 0.001 g prior to use.

7.3.2 Weigh a well-mixed sample to the nearest 0.001 g into the fluorocarbon sample vessel equipped with a single-ported cap and a pressure relief valve. For soils, sediments, and sludges use no more than 0.500 g. For oils use no more than 0.250 g.

7.3.3 Add 10 ± 0.1 mL concentrated nitric acid in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and torque the cap to 12 ft-lbs (16 N-m) or according to the unit manufacturer's directions. Weigh the vessels to the nearest 0.001 g. Place the vessels in the microwave carousel.

CAUTION: Toxic nitrogen oxide fumes may be evolved, therefore all work must be performed in a properly operating ventilation system. The analyst should also be aware of the potential for a vigorous reaction. If a vigorous reaction occurs, allow to cool before capping the vessel.

CAUTION: When digesting samples containing volatile or easily oxidized organic compounds, initially weigh no more than 0.10 g and observe the reaction before capping the vessel. If a vigorous reaction occurs, allow the reaction to cease before capping the vessel. If no appreciable reaction occurs, a sample weight up to 0.25 g can be used.

CAUTION: All samples known or suspected of containing more than 5-10% organic material should be predigested in a hood for at least 15 minutes.

7.3.4 Properly place the carousel in the microwave unit according to the manufacturer's recommended specifications and, if used, connect the pressure vessels to the central overflow vessel with PFA-fluorocarbon tubes. Any vessels containing 10 mL of nitric acid for analytical blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, the remaining vessels should be filled with 10 mL of nitric acid to achieve the full complement of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity (Ref. 4). Irradiate each group of sample vessels for 10 minutes. The temperature of each sample should rise to 175 °C in less than 5.5 minutes and remain between 170-180 °C for the balance of the 10 minute irradiation period. The pressure should peak at less than 6 atm for most soil, sludge, and sediment samples (Ref. 5). The pressure will exceed these limits in the case of high concentrations of carbonate or organic compounds. In these cases the pressure will be limited by the relief pressure of the vessel to 7.5 ± 0.7 atm (110 ± 10 psi). All vessels should be sealed according to the manufacturers recommended specifications.

7.3.4.1 Newer microwave units are capable of higher power (W) that permits digestion of a larger number of samples per batch. If the analyst wishes to digest more samples at a time, the analyst may use different values of power as long as they result in the same time and temperature conditions defined in 7.3.4. That is, any sequence of power that brings the samples to 175°C in 5.5 minutes and permits a slow rise to 175 - 180°C during the remaining 4.5 minutes (Ref. 5).

Issues of safety, structural integrity (both temperature and pressure limitations), heat loss, chemical compatibility, microwave absorption of vessel material, and energy transport will be considerations made in choosing alternative vessels. If all of the considerations are met and the appropriate power settings provided to reproduce the reaction conditions defined in 7.3.4, then these alternative vessels may be used (Ref. 1,2).

7.3.5 At the end of the microwave program, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave unit. When the vessels have cooled to room temperature, weigh and record the weight of each vessel assembly. If the weight of acid plus sample has decreased by more than 10 percent from the original weight, discard the sample. Determine the reason for the weight loss. These are typically attributed to loss of vessel seal integrity, use of a digestion time longer than 10 minutes, too large a sample, or improper heating conditions. Once the source of the loss has been corrected, prepare a new sample or set of samples for digestion beginning at 7.3.1.

7.3.6 Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered.

7.3.6.1 Centrifugation: Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.3.6.2 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

7.3.6.3 Filtering: The filtering apparatus must be thoroughly cleaned and prerinsed with dilute (approximately 10% V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned container.

7.3.7 Dilute the digest to a known volume ensuring that the samples and standards are matrix matched. The digest is now ready for analysis for elements of interest using the appropriate SW-846 method.

7.4 Calculations: The concentrations determined are to be reported on the basis of the actual weight of the original sample.

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by, or under supervision of, experienced analysts. Refer to the appropriate section of Chapter One for additional quality control guidance.

8.2 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analytical process. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number. A duplicate sample should be prepared for each matrix type (i.e., soil, sludge, etc.).

8.3 Spiked samples or standard reference materials should be included with each group of samples processed or every 20 samples, whichever is the greater number. A spiked sample should also be included whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision: Precision data for Method 3051, as determined by the statistical examination of interlaboratory test results, is located in Tables 1 and 2.

9.2 Repeatability: If successive results are obtained by the same analyst with the same apparatus under constant operating conditions on identical test material, then the difference between these successive results will not, with 95% probability, exceed the repeatability value. For example, in the case of lead, an average of only 1 case in 20 would exceed

$$0.206\ x$$

in the long run, where x is one result in μg/g (Ref. 6).

9.3 Reproducibility: If two successive measurements are made independently by each of two different analysts working in different laboratories on identical test material, then the difference between the average result for each analyst will not, with 95% probability, exceed the reproducibility value. For example, in the case of lead, an average of only 1 case in 20 would exceed

$$0.303\ x$$

in the long run, where x is the average of two successive measurements in μg/g (Ref. 2).

As can be seen in Table 1, repeatability and reproducibility differ between elements, and usually depend on that element's concentration. Table 2 provides an example of how users of the method can determine expected values for repeatability and reproducibility; nominal values of lead have been used for this model (Ref. 6).

9.4 Bias: In the case of SRM 1085 - Wear Metals in Oil, the bias of this test method is different for each element. An estimate of bias, as shown in Table 3, is:

$$\text{Bias} = \text{Amount found} - \text{Amount expected.}$$

However, the bias estimate inherits both the uncertainty in the measurements made using Method 3051 and the uncertainty on the certificate, so whether the bias is real or only due to measurement error must also be considered. The concentrations found for Al, Cr, and Cu using Method 3051 fall within their certified ranges on SRM 1085, and 95% confidence intervals for Fe and Ni overlap with their respective certified ranges; therefore, the observed biases for these elements are probably due to chance and should be considered insignificant. Biases should not be estimated at all for Ag and Pb because these elements were not certified. Therefore, the only two elements considered in this table for which the bias estimates are significant are Mg and Mo.

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TABLE 1.
EQUATIONS RELATING REPEATABILITY AND REPRODUCIBILITY TO MEAN CONCENTRATION OF DUPLICATE DETERMINATION WITH 95 PERCENT CONFIDENCE

Element	Repeatability	Reproducibility
Ag	0.195X[a]	0.314X
Al	0.232X	0.444X
B	12.9[b]	22.6[b]
Ba	0.238X	0.421X
Be	0.082[b]	0.082[b]
Ca	0.356X	1.27X
Cd	0.385X	0.571X
Co	0.291X	0.529X
Cr	0.187X	0.195X
Cu	0.212X	0.322X
Fe	0.257X	0.348X
Mg	0.238X	0.399X
Mn	1.96X1/2[c]	4.02X1/2
Mo	0.701X	0.857X
Ni	0.212X	0.390X
Pb	0.206X	0.303X
Sr	0.283X	0.368X
V	1.03X1/2	2.23X1/2
Zn	3.82X1/2	7.69X1/2

[a]Log transformed variable based on one-way analysis of variance.
[b]Repeatability and reproducibility were independent of concentration.
[c]Square root transformed variable based on one-way analysis of variance.

TABLE 2.
REPEATABILITY AND REPRODUCIBILITY FOR LEAD
BY METHOD 3051

Average Value	Repeatability	Reproducibility
50	10.3	15.2
100	20.6	30.3
200	41.2	60.6
300	61.8	90.9
400	82.4	121
500	103	152

All results are in mg/Kg

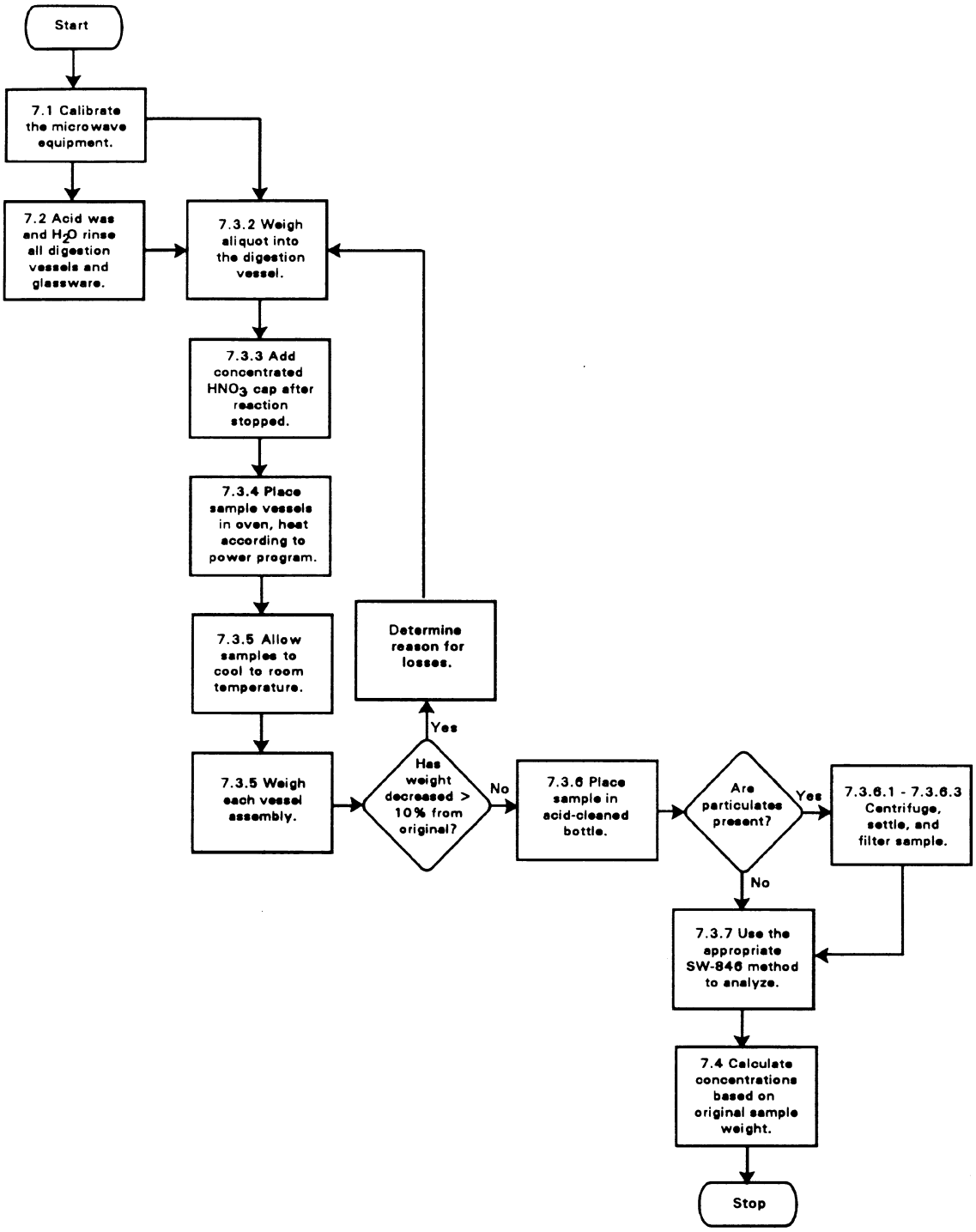
TABLE 3.
RECOVERY AND BIAS DATA FOR SRM 1085 - WEAR METALS IN OIL

Element	Amount Expected (Certified Range)	Amount Found* (95% Conf Interval)	Absolute Bias (µg/g)	Relative Bias (Percent)	Significant (due to more than chance)
Ag	(291)**	234±16	--	--	--
Al	296±4	295±12	-1	0	No
Cr	298±5	293±10	-5	-2	No
Cu	295±10	289±9	-6	-2	No
Fe	300±4	311±14	+11	+4	No
Mg	297±3	270±11	-27	-9	Yes
Mo	292±11	238±11	-54	-18	Yes
Mi	303±7	293±9	-10	-3	No
Pb	(305)**	279±8	--	--	--

All values in mg/Kg

*Results taken from table 4-7, Ref. 2.

**Value not certified, so should not be used in bias detection and estimation.


Start
7.1 Calibrate the microwave equipment.
7.2 Acid was and H_2O rinse all digestion vessels and glassware.
7.3.2 Weigh aliquot into the digestion vessel.
7.3.3 Add concentrated HNO_3 cap after reaction stopped.
7.3.4 Place sample vessels in oven, heat according to power program.
7.3.5 Allow samples to cool to room temperature.
7.3.5 Weigh each vessel assembly.
Has weight decreased > 10% from original?
Yes
Determine reason for losses.
No
7.3.6 Place sample in acid-cleaned bottle.
Are particulates present?
Yes
7.3.6.1 - 7.3.6.3 Centrifuge, settle, and filter sample.
No
7.3.7 Use the appropriate SW-846 method to analyze.
7.4 Calculate concentrations based on original sample weight.
Stop

METHOD 6010B

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) determines trace elements, including metals, in solution. The method is applicable to all of the elements listed in Table 1. All matrices, excluding filtered groundwater samples but including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis. Groundwater samples that have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards. Refer to Chapter Three for the appropriate digestion procedures.

1.2 Table 1 lists the elements for which this method is applicable. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. Table 1 lists the recommended analytical wavelengths and estimated instrumental detection limits for the elements in clean aqueous matrices. The instrument detection limit data may be used to estimate instrument and method performance for other sample matrices. Elements and matrices other than those listed in Table 1 may be analyzed by this method if performance at the concentration levels of interest (see Section 8.0) is demonstrated.

1.3 Users of the method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using the method for analysis.

1.4 Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences described in this method.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g. Chapter Three). When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 This method describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used should be as free as possible from spectral interference and should reflect the same change in background

intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 3.0 should also be recognized and appropriate corrections made; tests for their presence are described in Section 8.5. Alternatively, users may choose multivariate calibration methods. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

3.0 INTERFERENCES

3.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

3.1.1 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.

3.1.2 To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient; however, for analytes such as iron that may be found at high concentration, a more appropriate test would be to use a concentration near the upper analytical range limit.

3.1.3 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction **require** the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement

correction equations determined on their instruments with tested concentration ranges to compensate (off line or on line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelengths are given in Table 2. For multivariate methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

3.1.4 When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary.

3.1.5 Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.

3.1.6 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences (Table 2) as well as any other suspected interferences that may be specific to the instrument or matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses.

3.1.7 Users of sequential instruments must verify the absence of spectral interference by scanning over a range of 0.5 nm centered on the wavelength of interest for several samples. The range for lead, for example, would be from 220.6 to 220.1 nm. This procedure must be repeated whenever a new matrix is to be analyzed and when a new calibration curve using different instrumental conditions is to be prepared. Samples that show an elevated background emission across the range may be background corrected by applying a correction factor equal to the emission adjacent to the line or at two points on either side of the line and interpolating between them. An alternate wavelength that does not exhibit a background shift or spectral overlap may also be used.

3.1.8 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and divided by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

3.1.9 When interelement corrections are applied, their accuracy should be verified, daily, by analyzing spectral interference check solutions. If the correction factors or multivariate correction matrices tested on a daily basis are found to be within the 20% criteria for 5 consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such they do not contain concentrations of the interfering elements at ± one reporting limit from zero, daily verification is not required. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change, such as in the torch, nebulizer, injector, or plasma conditions occurs. Standard solution should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

3.1.10 When interelement corrections are <u>not</u> used, verification of absence of interferences is required.

3.1.10.1 One method is to use a computer software routine for comparing the determinative data to limits files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration, (i.e., greater than) the analyte instrument detection limit, or false negative analyte concentration, (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval).

3.1.10.2 Another method is to analyze an Interference Check Solution(s) which contains similar concentrations of the major components of the samples (>10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is $\geq$ 20% of the analyte concentration, the analyte must be determined using (1) analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

3.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump, by using an internal standard or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate

and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, using a high solids nebulizer or diluting the sample. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance: this may be accomplished with the use of mass flow controllers. The test described in Section 8.5.1 will help determine if a physical interference is present.

3.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

3.4 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit should be noted. Until the required rinse time is established, this method suggests a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon their DQOs.

3.5 Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

3.6 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled argon plasma emission spectrometer:

4.1.1 Computer-controlled emission spectrometer with background correction.

4.1.2 Radio-frequency generator compliant with FCC regulations.

4.1.3 Optional mass flow controller for argon nebulizer gas supply.

4.1.4 Optional peristaltic pump.

4.1.5 Optional Autosampler.

4.1.6 Argon gas supply - high purity.

4.2 Volumetric flasks of suitable precision and accuracy.

4.3 Volumetric pipets of suitable precision and accuracy.

5.0 REAGENTS

5.1 Reagent or trace metals grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question analyze for contamination. If the concentration of the contamination is less than the MDL then the reagent is acceptable.

5.1.1 Hydrochloric acid (conc), HCl.

5.1.2 Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL water and dilute to 1 liter in an appropriately sized beaker.

5.1.3 Nitric acid (conc), HNO_3.

5.1.4 Nitric acid (1:1), HNO_3. Add 500 mL concentrated HNO_3 to 400 mL water and dilute to 1 liter in an appropriately sized beaker.

5.2 Reagent Water. All references to water in the method refer to reagent water unless otherwise specified. Reagent water will be interference free. Refer to Chapter One for a definition of reagent water.

5.3 Standard stock solutions may be purchased or prepared from ultra- high purity grade chemicals or metals (99.99% pure or greater). All salts must be dried for 1 hour at 105°C, unless otherwise specified.

Note: This section does not apply when analyzing samples that have been prepared by Method 3040.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the element fraction and the weight of the metal salt added.

For metals:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

For metal salts:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg) x mole fraction}}{\text{volume (L)}}$$

5.3.1 Aluminum solution, stock, 1 mL = 1000 µg Al: Dissolve 1.000 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4.0 mL of (1:1) HCl and 1.0 mL of concentrated $HN0_3$ in a beaker. Warm beaker slowly to effect solution. When dissolution is complete, transfer solution quantitatively to a 1-liter flask, add an additional 10.0 mL of (1:1) HCl and dilute to volume with reagent water.

NOTE: Weight of analyte is expressed to four significant figures for consistency with the weights below because rounding to two decimal places can contribute up to 4 % error for some of the compounds.

5.3.2 Antimony solution, stock, 1 mL = 1000 µg Sb: Dissolve 2.6673 g $K(SbO)C_4H_4O_6$ (element fraction Sb = 0.3749), weighed accurately to at least four significant figures, in water, add 10 mL (1:1) HCl, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.3 Arsenic solution, stock, 1 mL = 1000 µg As: Dissolve 1.3203 g of As_2O_3 (element fraction As = 0.7574), weighed accurately to at least four significant figures, in 100 mL of water containing 0.4 g NaOH. Acidify the solution with 2 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.4 Barium solution, stock, 1 mL = 1000 µg Ba: Dissolve 1.5163 g $BaCl_2$ (element fraction Ba = 0.6595), dried at 250°C for 2 hours, weighed accurately to at least four significant figures, in 10 mL water with 1 mL (1:1) HCl. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.5 Beryllium solution, stock, 1 mL = 1000 µg Be: Do not dry. Dissolve 19.6463 g $BeSO_4{\cdot}4H_2O$ (element fraction Be = 0.0509), weighed accurately to at least four significant figures, in water, add 10.0 mL concentrated HNO_3, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.6 Boron solution, stock, 1 mL = 1000 µg B: Do not dry. Dissolve 5.716 g anhydrous H_3BO_3 (B fraction = 0.1749), weighed accurately to at least four significant figures, in reagent water and dilute in a 1-L volumetric flask with reagent water. Transfer immediately after mixing in a clean polytetrafluoroethylene (PTFE) bottle to minimize any leaching of boron from the glass volumetric container. Use of a non-glass volumetric flask is recommended to avoid boron contamination from glassware.

5.3.7 Cadmium solution, stock, 1 mL = 1000 µg Cd: Dissolve 1.1423 g CdO (element fraction Cd = 0.8754), weighed accurately to at least four significant figures, in a

minimum amount of (1:1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.8 Calcium solution, stock, 1 mL = 1000 µg Ca: Suspend 2.4969 g $CaCO_3$ (element Ca fraction = 0.4005), dried at 180°C for 1 hour before weighing, weighed accurately to at least four significant figures, in water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.9 Chromium solution, stock, 1 mL = 1000 µg Cr: Dissolve 1.9231 g CrO_3 (element fraction Cr = 0.5200), weighed accurately to at least four significant figures, in water. When solution is complete, acidify with 10 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.10 Cobalt solution, stock, 1 mL = 1000 µg Co: Dissolve 1.00 g of cobalt metal, weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.11 Copper solution, stock, 1 mL = 1000 µg Cu: Dissolve 1.2564 g CuO (element fraction Cu = 0.7989), weighed accurately to at least four significant figures), in a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.12 Iron solution, stock, 1 mL = 1000 µg Fe: Dissolve 1.4298 g Fe_2O_3 (element fraction Fe = 0.6994), weighed accurately to at least four significant figures, in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated HNO_3. Cool, add an additional 5.0 mL of concentrated HNO_3, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.13 Lead solution, stock, 1 mL = 1000 µg Pb: Dissolve 1.5985 g $Pb(NO_3)_2$ (element fraction Pb = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10 mL (1:1) HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.14 Lithium solution, stock, 1 mL = 1000 µg Li: Dissolve 5.3248 g lithium carbonate (element fraction Li = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.15 Magnesium solution, stock, 1 mL = 1000 µg Mg: Dissolve 1.6584 g MgO (element fraction Mg = 0.6030), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.16 Manganese solution, stock, 1 mL = 1000 µg Mn: Dissolve 1.00 g of manganese metal, weighed accurately to at least four significant figures, in acid mixture (10 mL concentrated HCl and 1 mL concentrated HNO_3) and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.17 Mercury solution, stock, 1 mL = 1000 µg Hg: Do not dry, highly toxic element. Dissolve 1.354 g $HgCl_2$ (Hg fraction = 0.7388) in reagent water. Add 50.0 mL concentrated HNO_3 and dilute to volume in 1-L volumetric flask with reagent water.

5.3.18 Molybdenum solution, stock, 1 mL = 1000 µg Mo: Dissolve 1.7325 g $(NH_4)_6Mo_7O_{24}.4H_2O$ (element fraction Mo = 0.5772), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.19 Nickel solution, stock, 1 mL = 1000 µg Ni: Dissolve 1.00 g of nickel metal, weighed accurately to at least four significant figures, in 10.0 mL hot concentrated HNO_3, cool, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.20 Phosphate solution, stock, 1 mL = 1000 µg P: Dissolve 4.3937 g anhydrous KH_2PO_4 (element fraction P = 0.2276), weighed accurately to at least four significant figures, in water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.21 Potassium solution, stock, 1 mL = 1000 µg K: Dissolve 1.9069 g KCl (element fraction K = 0.5244) dried at 110°C, weighed accurately to at least four significant figures, in water, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.22 Selenium solution, stock, 1 mL = 1000 µg Se: Do not dry. Dissolve 1.6332 g H_2SeO_3 (element fraction Se = 0.6123), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.23 Silica solution, stock, 1 mL = 1000 µg SiO_2: Do not dry. Dissolve 2.964 g NH_4SiF_6, weighed accurately to at least four significant figures, in 200 mL (1:20) HCl with heating at 85°C to effect dissolution. Let solution cool and dilute to volume in a 1-L volumetric flask with reagent water.

5.3.24 Silver solution, stock, 1 mL = 1000 µg Ag: Dissolve 1.5748 g $AgNO_3$ (element fraction Ag = 0.6350), weighed accurately to at least four significant figures, in water and 10 mL concentrated HNO_3. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.25 Sodium solution, stock, 1 mL = 1000 µg Na: Dissolve 2.5419 g NaCl (element fraction Na = 0.3934), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.26 Strontium solution, stock, 1 mL = 1000 µg Sr: Dissolve 2.4154 g of strontium nitrate ($Sr(NO_3)_2$) (element fraction Sr = 0.4140), weighed accurately to at least four significant figures, in a 1-liter flask containing 10 mL of concentrated HCl and 700 mL of water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.27 Thallium solution, stock, 1 mL = 1000 µg Tl: Dissolve 1.3034 g $TlNO_3$ (element fraction Tl = 0.7672), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.28 Tin solution, stock, 1 mL = 1000 µg Sn: Dissolve 1.000 g Sn shot, weighed accurately to at least 4 significant figures, in 200 mL (1:1) HCl with heating to effect dissolution. Let solution cool and dilute with (1:1) HCl in a 1-L volumetric flask.

5.3.29 Vanadium solution, stock, 1 mL = 1000 µg V: Dissolve 2.2957 g NH_4VO_3 (element fraction V = 0.4356), weighed accurately to at least four significant figures, in a minimum amount of concentrated HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.30 Zinc solution, stock, 1 mL = 1000 µg Zn: Dissolve 1.2447 g ZnO (element fraction Zn = 0.8034), weighed accurately to at least four significant figures, in a minimum amount of dilute HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.4 Mixed calibration standard solutions - Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Table 3). Add the appropriate types and volumes of acids so that the standards are matrix matched with the sample digestates. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Some typical calibration standard combinations are listed in Table 3.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

5.5 Two types of blanks are required for the analysis for samples prepared by any method other than 3040. The calibration blank is used in establishing the analytical curve, and the method blank is used to identify possible contamination resulting from varying amounts of the acids used in the sample processing.

5.5.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples. The calibration blank will also be used for all initial and continuing calibration blank determinations (see Sections 7.3 and 7.4).

5.5.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.6 The Initial Calibration Verification (ICV) is prepared by the analyst by combining compatible elements from a standard source different than that of the calibration standard and at concentrations within the linear working range of the instrument (see Section 8.6.1 for use).

5.7 The Continuing Calibration Verification (CCV)) should be prepared in the same acid matrix using the same standards used for calibration at a concentration near the mid-point of the calibration curve (see Section 8.6.1 for use).

5.8 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest, particularly those with known interferences at 0.5 to 1 mg/L. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Inorganic Analytes, Sections 3.1 through 3.3.

7.0 PROCEDURE

7.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater samples which have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards**.** Solubilization and digestion procedures are presented in Sample Preparation Methods (Chapter Three, Inorganic Analytes).

7.2 Set up the instrument with proper operating parameters established as detailed below. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration). Operating conditions - The analyst should follow the instructions provided by the instrument manufacturer.

7.2.1 Before using this procedure to analyze samples, there must be data available documenting initial demonstration of performance. The required data document the selection criteria of background correction points; analytical dynamic ranges, the applicable equations, and the upper limits of those ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. This data must be generated using the same instrument, operating conditions and calibration routine to be used for sample analysis. These documented data must be kept on file and be available for review by the data user or auditor.

7.2.2 Specific wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of spectrometers, specific instrument operating conditions cannot be provided. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for

a task. Operating conditions for aqueous solutions usually vary from 1100 to 1200 watts forward power, 14 to 18 mm viewing height, 15 to 19 liters/min argon coolant flow, 0.6 to 1.5 L/min argon nebulizer flow, 1 to 1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 second per wavelength peak for sequential instruments and 10 seconds per sample for simultaneous instruments. For an axial plasma, the conditions will usually vary from 1100-1500 watts forward power, 15-19 liters/min argon coolant flow, 0.6-1.5 L/min argon nebulizer flow, 1-1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 second per wavelength peak for sequential instruments and 10 seconds per sample for simultaneous instruments. Reproduction of the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm respectively, by adjusting the argon aerosol flow has been recommended as a way to achieve repeatable interference correction factors.

7.2.3 The plasma operating conditions need to be optimized prior to use of the instrument. This routine is not required on a daily basis, but only when first setting up a new instrument or following a change in operating conditions. The following procedure is recommended or follow manufacturer's recommendations. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure.

7.2.3.1 Ignite the radial plasma and select an appropriate incident RF power. Allow the instrument to become thermally stable before beginning, about 30 to 60 minutes of operation. While aspirating a 1000 ug/L solution of yttrium, follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the load coil. Record the nebulizer gas flow rate or pressure setting for future reference. The yttrium solution can also be used for coarse optical alignment of the torch by observing the overlay of the blue light over the entrance slit to the optical system.

7.2.3.2 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min by aspirating a known volume of calibration blank for a period of at least three minutes. Divide the volume aspirated by the time in minutes and record the uptake rate; set the peristaltic pump to deliver the rate in a steady even flow.

7.2.3.3 Profile the instrument to align it optically as it will be used during analysis. The following procedure can be used for both horizontal and vertical optimization in the radial mode, but is written for vertical. Aspirate a solution containing 10 ug/L of several selected elements. These elements can be As, Se, Tl or Pb as the least sensitive of the elements and most needing to be optimize or others representing analytical judgement (V, Cr, Cu, Li and Mn are also used with success). Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14 to 18 mm above the load coil. (This region of the plasma is referred to as the analytical zone.) Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the best net intensity ratios for the elements analyzed or the highest intensity ratio for the least

sensitive element. For optimization in the axial mode, follow the instrument manufacturer's instructions.

7.2.3.4 The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits and method detection limits.

7.2.3.5 If either the instrument operating conditions, such as incident power or nebulizer gas flow rate are changed, or a new torch injector tube with a different orifice internal diameter is installed, the plasma and viewing height should be re-optimized.

7.2.3.6 After completing the initial optimization of operating conditions, but before analyzing samples, the laboratory must establish and initially verify an interelement spectral interference correction routine to be used during sample analysis. A general description concerning spectral interference and the analytical requirements for background correction in particular are discussed in the section on interferences. Criteria for determining an interelement spectral interference is an apparent positive or negative concentration for the analyte that falls within ± one reporting limit from zero. The upper control limit is the analyte instrument detection limit. Once established the entire routine must be periodically verified every six months. Only a portion of the correction routine must be verified more frequently or on a daily basis. Initial and periodic verification of the routine should be kept on file. Special cases where continual verification is required are described elsewhere.

7.2.3.7 Before daily calibration and after the instrument warmup period, the nebulizer gas flow rate must be reset to the determined optimized flow. If a mass flow controller is being used, it should be set to the recorded optimized flow rate, In order to maintain valid spectral interelement correction routines the nebulizer gas flow rate should be the same (< 2% change) from day to day.

7.2.4 For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements.

7.2.5 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.

7.2.5.1 Method detection limits must be established for all wavelengths utilized for each type of matrix commonly analyzed. The matrix used for the MDL calculation must contain analytes of known concentrations within 3-5 times the anticipated detection limit. Refer to Chapter One for additional guidance on the performance of MDL studies.

7.2.5.2 Determination of limits using reagent water represent a best case situation and do not represent possible matrix effects of real world samples.

7.2.5.3 If additional confirmation is desired, reanalyze the seven replicate aliquots on two more non consecutive days and again calculate the method detection limit values for each day. An average of the three values for each analyte may provide for a more appropriate estimate. Successful analysis of samples with added analytes or using method of standard additions can give confidence in the method detection limit values determined in reagent water.

7.2.5.4 The upper limit of the linear dynamic range must be established for each wavelength utilized by determining the signal responses from a minimum for three, preferably five, different concentration standards across the range. One of these should be near the upper limit of the range. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file. The upper range limit should be an observed signal no more than 10% below the level extrapolated from lower standards. Determined analyte concentrations that are above the upper range limit must be diluted and reanalyzed. The analyst should also be aware that if an interelement correction from an analyte above the linear range exists, a second analyte where the interelement correction has been applied may be inaccurately reported. New dynamic ranges should be determined whenever there is a significant change in instrument response. For those analytes that periodically approach the upper limit, the range should be checked every six months. For those analytes that are known interferences, and are present at above the linear range, the analyst should ensure that the interelement correction has not been inaccurately applied.

NOTE: Many of the alkali and alkaline earth metals have non-linear response curves due to ionization and self absorption effects. These curves may be used if the instrument allows; however the effective range must be checked and the second order curve fit should have a correlation coefficient of 0.995 or better. Third order fits are not acceptable. These non-linear response curves should be revalidated and recalculated every six months. These curves are much more sensitive to changes in operating conditions than the linear lines and should be checked whenever there have been moderate equipment changes.

7.2.6 The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

7.3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 5.4. Flush the system with the calibration blank (Section 5.5.1) between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve must consist of a minimum of a blank and a standard.

7.4 For all analytes and determinations, the laboratory must analyze an ICV (Section 5.6), a calibration blank (Section 5.5.1), and a continuing calibration verification (CCV) (Section 5.7) immediately following daily calibration. A calibration blank and either a calibration verification (CCV) or an ICV must be analyzed after every tenth sample and at the end of the sample run. Analysis of

the check standard and calibration verification must verify that the instrument is within ± 10% of calibration with relative standard deviation < 5% from replicate (minimum of two) integrations. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable ICV, CCV or check standard must be reanalyzed. The analysis data of the calibration blank, check standard, and ICV or CCV must be kept on file with the sample analysis data.

7.5 Rinse the system with the calibration blank solution (Section 5.5.1) before the analysis of each sample. The rinse time will be one minute. Each laboratory may establish a reduction in this rinse time through a suitable demonstration.

7.6 Calculations: If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported with up to three significant figures.

7.7 The MSA should be used if an interference is suspected or a new matrix is encountered. When the method of standard additions is used, standards are added at one or more levels to portions of a prepared sample. This technique compensates for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences, such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added; while to the second aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated by: multiplying the intensity value for the unfortified aliquot by the volume (Liters) and concentration (mg/L or mg/kg) of the standard addition to make the numerator; the difference in intensities for the fortified sample and unfortified sample is multiplied by the volume (Liters) of the sample aliquot for the denominator. The quotient is the sample concentration.

For more than one fortified portion of the prepared sample, linear regression analysis can be applied using a computer or calculator program to obtain the concentration of the sample solution.

NOTE: Refer to Method 7000 for a more detailed discussion of the MSA.

7.8 An alternative to using the method of standard additions is the internal standard technique. Add one or more elements not in the samples and verified not to cause an interelement spectral interference to the samples, standards and blanks; yttrium or scandium are often used. The concentration should be sufficient for optimum precision but not so high as to alter the salt concentration of the matrix. The element intensity is used by the instrument as an internal standard to ratio the analyte intensity signals for both calibration and quantitation. This technique is very useful in overcoming matrix interferences especially in high solids matrices.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. All quality control measures described in Chapter One should be followed.

8.2 Dilute and reanalyze samples that exceed the linear calibration range or use an alternate, less sensitive line for which quality control data is already established.

8.3 Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank is a volume of reagent water carried through the same preparation process as a sample (refer to Chapter One).

8.4 Analyze matrix spiked duplicate samples at a frequency of one per matrix batch. A matrix duplicate sample is a sample brought through the entire sample preparation and analytical process in duplicate.

8.4.1.1 The relative percent difference between spiked matrix duplicate determinations is to be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(|D_1 + D_2|)/2} \times 100$$

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (replicate).

(A control limit of ± 20% RPD or within the documented historical acceptance limits for each matrix shall be used for sample values greater than ten times the instrument detection limit.)

8.4.1.2 The spiked sample or spiked duplicate sample recovery is to be within ± 25% of the actual value or within the documented historical acceptance limits for each matrix.

8.5 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in Sections 8.5.1 and 8.5.2, will ensure that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

8.5.1 Dilution Test: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

8.5.2 Post Digestion Spike Addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

CAUTION: If spectral overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

8.6 Check the instrument standardization by analyzing appropriate QC samples as follows.

8.6.1 Verify calibration with the Continuing Calibration Verification (CCV) Standard immediately following daily calibration, after every ten samples, and at the end of an analytical run. Check calibration with an ICV following the initial calibration (Section 5.6). At the laboratory's discretion, an ICV may be used in lieu of the continuing calibration verifications. If used in this manner, the ICV should be at a concentration near the mid-point of the calibration curve. Use a calibration blank (Section 5.5.1) immediately following daily calibration, after every 10 samples and at the end of the analytical run.

8.6.1.1 The results of the ICV and CCVs are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.6.1.2 The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.6.1.3 The results of the calibration blank are to agree within three times the IDL. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within ten percent of the action limit, analyses need not be rerun and recalibration need not be performed before continuation of the run.

8.6.2 Verify the interelement and background correction factors at the beginning of each analytical run. Do this by analyzing the interference check sample (Section 5.8). Results should be within ± 20% of the true value.

9.0 METHOD PERFORMANCE

9.1 In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

9.2 Performance data for aqueous solutions and solid samples from a multilaboratory study (9) are provided in Tables 5 and 6.

10.0 REFERENCES

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5. Jones, C.L. et al. An Interlaboratory Study of Inductively Coupled Plasma Atomic Emission Spectroscopy Method 6010 and Digestion Method 3050. EPA-600/4-87-032, U.S. Environmental Protection Agency, Las Vegas, Nevada, 1987.

TABLE 1
RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Detection Element	Wavelength[a] (nm)	Estimated IDL[b] (µg/L)
Aluminum	308.215	30
Antimony	206.833	21
Arsenic	193.696	35
Barium	455.403	0.87
Beryllium	313.042	0.18
Boron	249.678x2	3.8
Cadmium	226.502	2.3
Calcium	317.933	6.7
Chromium	267.716	4.7
Cobalt	228.616	4.7
Copper	324.754	3.6
Iron	259.940	4.1
Lead	220.353	28
Lithium	670.784	2.8
Magnesium	279.079	20
Manganese	257.610	0.93
Mercury	194.227x2	17
Molybdenum	202.030	5.3
Nickel	231.604x2	10
Phosphorus	213.618	51
Potassium	766.491	See note c
Selenium	196.026	50
Silica (SiO_2)	251.611	17
Silver	328.068	4.7
Sodium	588.995	19
Strontium	407.771	0.28
Thallium	190.864	27
Tin	189.980x2	17
Titanium	334.941	5.0
Vanadium	292.402	5.0
Zinc	213.856x2	1.2

[a]The wavelengths listed (where x2 indicates second order) are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted (e.g., in the case of an interference) if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Section 3.1). In time, other elements may be added as more information becomes available and as required.

[b]The estimated instrumental detection limits shown are provided as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

[c]Highly dependent on operating conditions and plasma position.

TABLE 2
POTENTIAL INTERFERENCES
ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM
INTERFERENCE AT THE 100-mg/L LEVEL[c]

Analyte	Wavelength (nm)	Interferant[a,b] Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

[a] Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al -	1000 mg/L	Mg -	1000 mg/L
Ca -	1000 mg/L	Mn -	200 mg/L
Cr -	200 mg/L	Tl -	200 mg/L
Cu -	200 mg/L	V -	200 mg/L
Fe -	1000 mg/L		

[b] The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

[c] Interferences will be affected by background choice and other interferences may be present.

TABLE 3
MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo
IV	Al, Ca, Cr, K, Na, Ni,Li, and Sr
V	Ag (see “NOTE” to Section 5.4), Mg, Sb, and Tl
VI	P

TABLE 4. ICP PRECISION AND ACCURACY DATA[a]

Element	Sample No. 1				Sample No. 2				Sample No. 3			
	True Conc. (ug/L)	Mean Conc. (ug/L)	RSD[b] (%)	Accuracy[d] (%)	True Conc. (ug/L)	Mean Conc. (ug/L)	RSD[b]	Accuracy[d] (%)	True Conc. (ug/L)	Mean Conc. (ug/L)	RSD[b] (%)	Accuracy[d] (%)
Be	750	733	6.2	98	20	20	9.8	100	180	176	5.2	98
Mn	350	345	2.7	99	15	15	6.7	100	100	99	3.3	99
V	750	749	1.8	100	70	69	2.9	99	170	169	1.1	99
As	200	208	7.5	104	22	19	23	86	60	63	17	105
Cr	150	149	3.8	99	10	10	18	100	50	50	3.3	100
Cu	250	235	5.1	94	11	11	40	100	70	67	7.9	96
Fe	600	594	3.0	99	20	19	15	95	180	178	6.0	99
Al	700	696	5.6	99	60	62	33	103	160	161	13	101
Cd	50	48	12	96	2.5	2.9	16	116	14	13	16	93
Co	700	512	10	73	20	20	4.1	100	120	108	21	90
Ni	250	245	5.8	98	30	28	11	93	60	55	14	92
Pb	250	236	16	94	24	30	32	125	80	80	14	100
Zn	200	201	5.6	100	16	19	45	119	80	82	9.4	102
Se[c]	40	32	21.9	80	6	8.5	42	142	10	8.5	8.3	85

[a] Not all elements were analyzed by all laboratories.
[b] RSD = relative standard deviation.
[c] Results for Se are from two laboratories.
[d] Accuracy is expressed as the mean concentration divided by the true concentration times 100.

TABLE 5

ICP-AES PRECISION AND ACCURACY FOR AQUEOUS SOLUTIONS[a]

Element	Mean Conc. (mg/L)	N[b]	RSD[b] (%)	Accuracy[c] (%)
Al	14.8	8	6.3	100
Sb	15.1	8	7.7	102
As	14.7	7	6.4	99
Ba	3.66	7	3.1	99
Be	3.78	8	5.8	102
Cd	3.61	8	7.0	97
Ca	15.0	8	7.4	101
Cr	3.75	8	8.2	101
Co	3.52	8	5.9	95
Cu	3.58	8	5.6	97
Fe	14.8	8	5.9	100
Pb	14.4	7	5.9	97
Mg	14.1	8	6.5	96
Mn	3.70	8	4.3	100
Mo	3.70	8	6.9	100
Ni	3.70	7	5.7	100
K	14.1	8	6.6	95
Se	15.3	8	7.5	104
Ag	3.69	6	9.1	100
Na	14.0	8	4.2	95
Tl	15.1	7	8.5	102
V	3.51	8	6.6	95
Zn	3.57	8	8.3	96

[a]these performance values are independent of sample preparation because the labs analyzed portions of the same solutions

[b]N = Number of measurements for mean and relative standard deviation (RSD).

[c]Accuracy is expressed as a percentage of the nominal value for each analyte in acidified, multi-element solutions.

TABLE 6

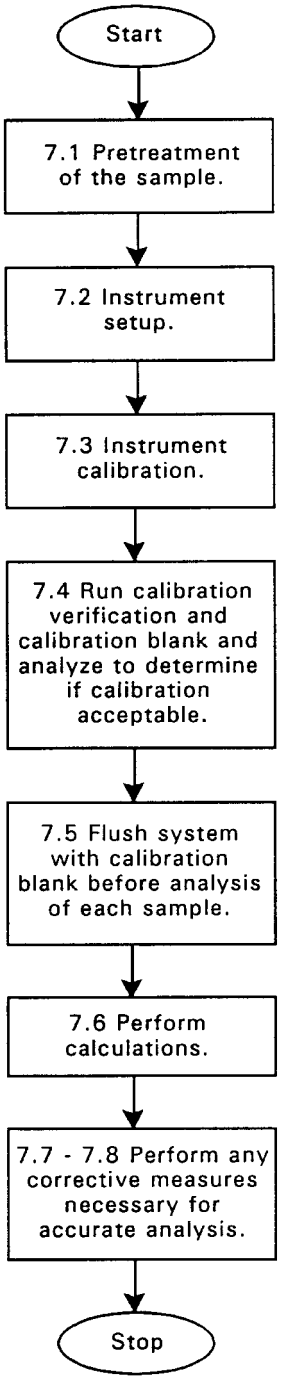
ICP-AES PRECISION AND BIAS FOR SOLID WASTE DIGESTS[a]

Element	Spiked Coal Fly Ash (NIST-SRM 1633a) Mean Conc. (mg/L)	N[b]	RSD[b] (%)	Bias[c] (%AAS)	Spiked Electroplating Sludge Mean Conc. (mg/L)	N[b]	RSD[b] (%)	Bias[c] (%AAS)
Al	330	8	16	104	127	8	13	110
Sb	3.4	6	73	96	5.3	7	24	120
As	21	8	83	270	5.2	7	8.6	87
Ba	133	8	8.7	101	1.6	8	20	58
Be	4.0	8	57	460	0.9	7	9.9	110
Cd	0.97	6	5.7	101	2.9	7	9.9	90
Ca	87	6	5.6	208	954	7	7.0	97
Cr	2.1	7	36	106	154	7	7.8	93
Co	1.2	6	21	94	1.0	7	11	85
Cu	1.9	6	9.7	118	156	8	7.8	97
Fe	602	8	8.8	102	603	7	5.6	98
Pb	4.6	7	22	94	25	7	5.6	98
Mg	15	8	15	110	35	8	20	84
Mn	1.8	7	14	104	5.9	7	9.6	95
Mo	891	8	19	105	1.4	7	36	110
Ni	1.6	6	8.1	91	9.5	7	9.6	90
K	46	8	4.2	98	51	8	5.8	82
Se	6.4	5	16	73	8.7	7	13	101
Ag	1.4	3	17	140	0.75	7	19	270
Na	20	8	49	130	1380	8	9.8	95
Tl	6.7	4	22	260	5.0	7	20	180
V	1010	5	7.5	100	1.2	6	11	80
Zn	2.2	6	7.6	93	266	7	2.5	101

[a]These performance values are independent of sample preparation because the labs analyzed portions of the same digests.

[b]N = Number of measurements for mean and relative standard deviation (RSD).

[c]Bias for the ICP-AES data is expressed as a percentage of atomic absorption spectroscopy (AA) data for the same digests.


Start
7.1 Pretreatment of the sample.
7.2 Instrument setup.
7.3 Instrument calibration.
7.4 Run calibration verification and calibration blank and analyze to determine if calibration acceptable.
7.5 Flush system with calibration blank before analysis of each sample.
7.6 Perform calculations.
7.7 - 7.8 Perform any corrective measures necessary for accurate analysis.
Stop

ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS FOR TOTAL METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis, by flame atomic absorption spectroscopy (FLAA) or inductively coupled argon plasma spectroscopy (ICP). The procedure is used to determine total metals.

1.2 Samples prepared by Method 3010 may be analyzed by FLAA or ICP for the following:

Aluminum	Magnesium
*Arsenic	Manganese
Barium	Molybdenum
Beryllium	Nickel
Cadmium	Potassium
Calcium	*Selenium
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

* Analysis by ICP

NOTE: See Method 7760 for the digestion and FLAA analysis of Silver.

1.3 This digestion procedure is not suitable for samples which will be analyzed by graphite furnace atomic absorption spectroscopy because hydrochloric acid can cause interferences during furnace atomization. Consult Method 3020A for samples requiring graphite furnace analysis.

2.0 SUMMARY OF METHOD

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with hydrochloric acid and brought up to volume. If sample should go to dryness, it must be discarded and the sample reprepared.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers - 150-mL or equivalent.

4.2 Watch glasses - Ribbed and plain or equivalent.

4.3 Qualitative filter paper or centrifugation equipment.

4.4 Graduated cylinder or equivalent - 100mL.

4.5 Funnel or equivalent.

4.6 Hot plate or equivalent heating source - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine levels of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (1:1), HCl. Prepared from water and hydrochloric acid. Hydrochloric acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Aqueous wastewaters must be acidified to a pH of < 2 with HNO_3.

7.0 PROCEDURE

7.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of concentrated HNO_3. Cover the beaker with

a ribbed watch glass or equivalent. Place the beaker on a hot plate or equivalent heating source and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Cover the beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If a sample is allowed to go to dryness, low recoveries will result. Should this occur, discard the sample and reprepare.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, uncover the beaker or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker. Add a small quantity of 1:1 HCl (10 mL/100 mL of final solution), cover the beaker, and reflux for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

7.3 Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned. Rinse the filter and filter apparatus with dilute nitric acid and discard the rinsate. Filter the sample and adjust the final volume to 100 mL with reagent water and the final acid concentration to 10%. The sample is now ready for analysis.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. A replicate sample should be processed with each analytical batch or every 20 samples, whichever is greater. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch of samples processed and whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spikes.

8.5 The method of standard addition shall be used for the analysis of all EP extracts and delisting petitions (see Method 7000, Step 8.7). Although not

required, use of the method of standard addition is recommended for any sample that is suspected of having an interference.

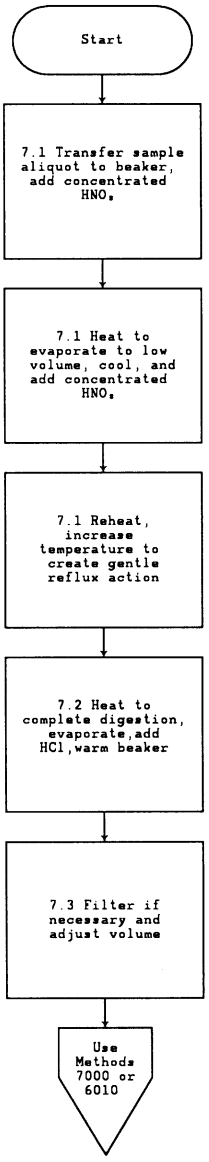
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.


Start
7.1 Transfer sample aliquot to beaker, add concentrated HNO3
7.1 Heat to evaporate to low volume, cool, and add concentrated HNO3
7.1 Reheat, increase temperature to create gentle reflux action
7.2 Heat to complete digestion, evaporate, add HCl, warm beaker
7.3 Filter if necessary and adjust volume
Use Methods 7000 or 6010

METHOD 3020A

ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS
FOR TOTAL METALS FOR ANALYSIS BY GFAA SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis by furnace atomic absorption spectroscopy (GFAA) for the metals listed below. The procedure is used to determine the total amount of the metal in the sample.

1.2 Samples prepared by Method 3020 may be analyzed by GFAA for the following metals:

Beryllium	Lead
Cadmium	Molybdenum
Chromium	Thallium
Cobalt	Vanadium

NOTE: For the digestion and GFAA analysis of arsenic and selenium, see Methods 7060 and 7740. For the digestion and GFAA analysis of silver, see Method 7761.

2.0 SUMMARY OF METHOD

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is cooled and brought up in dilute nitric acid such that the final dilution contains 3% (v/v) nitric acid. This percentage will vary depending on the amount of acid used to complete the digestion. If the sample contains suspended solids, it must be centrifuged, filtered, or allowed to settle.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers - 150-mL, or equivalent.

4.2 Watch glasses - ribbed or equivalent.

4.3 Qualitative filter paper or centrifugation equipment.

4.4 Funnel or equivalent.

4.5 Graduated Cylinder - 100mL.

4.6 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine levels of impurities. If method blank is < MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Aqueous wastewaters must be acidified to a pH of < 2 with HNO_3.

7.0 PROCEDURE

7.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass. Place the beaker on a hot plate and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Cover the beaker with a non-ribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). When the digestion is complete, evaporate to a low volume (3 mL); use a ribbed watch glass, not allowing any portion of the bottom of the beaker to go dry. Remove the beaker and add approximately 10 mL of water, mix, and continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.

7.3 Remove the beaker from the hot plate and wash down the beaker walls and watch glass with water. When necessary, filter or centrifuge the sample to remove silicates and other insoluble material that may interfere with injecting the sample into the graphite atomizer. (This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3.) Adjust to the final volume of 100 mL with water. The sample is now ready for analysis.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each batch of samples processed, method blanks should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. Replicate samples will be used to determine precision. The sample load will dictate frequency, but 5% is recommended. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch of samples processed or 5% and whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spikes.

8.5 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source. Refer to Chapter One for the proper protocol.

8.6 The method of standard addition shall be used for the analysis of all EP extracts. See Method 7000, Step 8.7, for further information.

9.0 METHOD PERFORMANCE

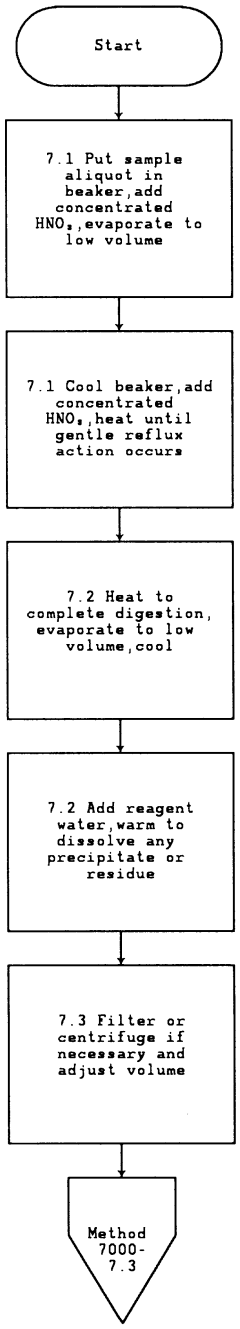
9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

METHOD 3020A
ACID DIGESTION FOR AQUEOUS SAMPLES AND EXTRACTS
FOR TOTAL METALS FOR ANALYSIS BY GFAA SPECTROSCOPY



METHOD 3052

MICROWAVE ASSISTED ACID DIGESTION OF SILICEOUS AND ORGANICALLY BASED MATRICES

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the microwave assisted acid digestion of siliceous matrices, and organic matrices and other complex matrices. If a total decomposition analysis (relative to the target analyte list) is required, the following matrices can be digested: ashes, biological tissues, oils, oil contaminated soils, sediments, sludges, and soils. This method is applicable for the following elements:

Aluminum	Cadmium	Iron	Molybdenum	Sodium
Antimony	Calcium	Lead	Nickel	Strontium
Arsenic	Chromium	Magnesium	Potassium	Thallium
Boron	Cobalt	Manganese	Selenium	Vanadium
Barium	Copper	Mercury	Silver	Zinc
Beryllium				

Other elements and matrices may be analyzed by this method if performance is demonstrated for the analyte of interest, in the matrices of interest, at the concentration levels of interest (see Sec. 8.0).

> Note: This technique is not appropriate for regulatory applications that require the use of leachate preparations (i.e., Method 3050, Method 3051, Method 1311, Method 1312, Method 1310, Method 1320, Method 1330, Method 3031, Method 3040). This method is appropriate for those applications requiring a total decomposition for research purposes (i.e., geological studies, mass balances, analysis of Standard Reference Materials) or in response to a regulation that requires total sample decomposition.

1.2 This method is provided as a rapid multi-element, microwave assisted acid digestion prior to analysis protocol so that decisions can be made about the site or material. Digests and alternative procedures produced by the method are suitable for analysis by flame atomic absorption spectrometry (FLAA), cold vapor atomic absorption spectrometry (CVAA), graphite furnace atomic absorption spectrometry (GFAA), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and other analytical elemental analysis techniques where applicable. Due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system and refer to this manual's "Disclaimer" when conducting analyses using Method 3052.

1.3 The goal of this method is total sample decomposition and with judicious choice of acid combinations this is achievable for most matrices (see Sec. 3.2). Selection of reagents which give the highest recoveries for the target analytes is considered the optimum method condition.

2.0 SUMMARY OF METHOD

2.1 A representative sample of up to 0.5 g is digested in 9 mL of concentrated nitric acid and usually 3 mL hydrofluoric acid for 15 minutes using microwave heating with a suitable laboratory microwave system. The method has several additional alternative acid and reagent combinations including hydrochloric acid and hydrogen peroxide. The method has provisions for scaling up the sample size to a maximum of 1.0 g. The sample and acid are placed in suitably inert polymeric microwave vessels. The vessel is sealed and heated in the microwave system. The temperature profile is specified to permit specific reactions and incorporates reaching 180 ± 5 ºC in approximately less than 5.5 minutes and remaining at 180 ± 5 ºC for 9.5 minutes for the completion of specific reactions (Ref. 1, 2, 3, 4). After cooling, the vessel contents may be filtered, centrifuged, or allowed to settle and then decanted, diluted to volume, and analyzed by the appropriate SW-846 method.

3.0 INTERFERENCES

3.1 Gaseous digestion reaction products, very reactive, or volatile materials that may create high pressures when heated and may cause venting of the vessels with potential loss of sample and analytes. The complete decomposition of either carbonates, or carbon based samples, may cause enough pressure to vent the vessel if the sample size is greater than 0.25 g. Variations of the method due to very reactive materials are specifically addressed in sections 7.3.4 and 7.3.6.1.

3.2 Most samples will be totally dissolved by this method with judicious choice of the acid combinations. A few refractory sample matrix compounds, such as TiO_2, alumina, and other oxides may not be totally dissolved and in some cases may sequester target analyte elements.

3.3 The use of several digestion reagents that are necessary to either completely decompose the matrix or to stabilize specific elements may limit the use of specific analytical instrumentation methods. Hydrochloric acid is known to interfere with some instrumental analysis methods such as flame atomic absorption (FLAA) and inductively coupled plasma atomic emission spectrometry (ICP-AES). The presence of hydrochloric acid may be problematic for graphite furnace atomic absorption (GFAA) and inductively coupled plasma mass spectrometry (ICP-MS). Hydrofluoric acid, which is capable of dissolving silicates, may require the removal of excess hydrofluoric acid or the use of specialized non-glass components during instrumental analysis. Method 3052 enables the analyst to select other decomposition reagents that may also cause problems with instrumental analyses necessitating matrix matching of standards to account for viscosity and chemical differences.

4.0 APPARATUS AND MATERIALS

4.1 Microwave apparatus requirements.

4.1.1 The temperature performance requirements necessitate the microwave decomposition system sense the temperature to within ± 2.5°C and automatically adjust the microwave field output power within 2 seconds of sensing. Temperature sensors should be accurate to ± 2°C (including the final reaction temperature of 180°C). Temperature feedback control provides the primary control performance mechanism for the method. Due to the flexibility in the reagents used to achieve total analysis, tempertuare feedback control is necessary for reproducible microwave heating.

Alternatively, for a specific set of reagent(s) combination(s), quantity, and specific vessel type, a calibration control mechanism can be developed similar to previous microwave methods (see Method 3051). Through calibration of the microwave power, vessel load and heat loss, the reaction temperature profile described in Section 7.3.6 can be reproduced. The calibration settings are specific for the number and type of vessel used and for the microwave system in addition to the variation in reagent combinations. Therefore no specific calibration settings are provided in this method. These settings may be developed by using temperature monitoring equipment for each specific set of equipment and reagent combination. They may only be used if not altered as previously described in other methods such as 3051 and 3015. In this circumstance, the microwave system provides programmable power which can be programmed to within ± 12 W of the required power. Typical systems provide a nominal 600 W to 1200 W of power (Ref. 1, 2, 5). Calibration control provides backward compatibility with older laboratory microwave systems without temperature monitoring or feedback control and with lower cost microwave systems for some repetitive analyses. Older lower pressure vessels may not be compatible.

4.1.2 The temperature measurement system should be periodically calibrated at an elevated temperature. Pour silicon oil (a high temperature oil into a beaker and adequately stirred to ensure a homogeneous temperature. Place the microwave temperature sensor and a calibrated external temperature measurement sensor into the beaker. Heat the beaker to a constant temperature of 180 ± 5°C. Measure the temperature with both sensors. If the measured temperatures vary by more than 1 - 2°C, the microwave temperature measurement system needs to be calibrated. Consult the microwave manufacturer's instructions about the specific temperature sensor calibration procedure.

> CAUTION: The use of microwave equipment with temperature feedback control is required to control the unfamiliar reactions of unique or untested reagent combinations of unknown samples. These tests may require additional vessel requirements such as increased pressure capabilities.

4.1.3 The microwave unit cavity is corrosion resistant and well ventilated. All electronics are protected against corrosion for safe operation.

> CAUTION: There are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. A listing of these specific suggestions is beyond the scope of this method and require the analyst to consult the specific equipment manual, manufacturer, and literature for proper and safe operation of the microwave equipment and vessels.

4.1.4 The method requires essentially microwave transparent and reagent resistant suitably inert polymeric materials (examples are PFA or TFM suitably inert polymeric polymers) to contain acids and samples. For higher pressure capabilities the vessel may be contained within layers of different microwave transparent materials for strength, durability, and safety. The vessels internal volume should be at least 45 mL, capable of withstanding pressures of at least 30 atm (30 bar or 435 psi), and capable of controlled pressure relief. These specifications are to provide an appropriate, safe, and durable reaction vessel of which there are many adequate designs by many suppliers.

CAUTION: The outer layers of vessels are frequently not as acid or reagent resistant as the liner material and must not be chemically degraded or physically damaged to retain the performance and safety required. Routine examination of the vessel materials may be required to ensure their safe use.

CAUTION: The second safety concern relates to the use of sealed containers without pressure relief devices. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures, but must be safely contained. However, many digestion vessels constructed from certain suitably inert polymerics may crack, burst, or explode in the unit under certain pressures. Only suitably inert polymeric (such as PFA or TFM and others) containers with pressure relief mechanisms or containers with suitably inert polymeric liners and pressure relief mechanisms are considered acceptable.

Users are therefore advised not to use domestic (kitchen) type microwave ovens or to use inappropriate sealed containers without pressure relief for microwave acid digestions by this method. Use of laboratory-grade microwave equipment is required to prevent safety hazards. For further details, consult Reference 3 and 6.

4.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within most systems (Ref. 1). The speed of the turntable should be a minimum of 3 rpm.

CAUTION: Laboratories should not use domestic (kitchen) type microwave ovens for this method. There are several significant safety issues. First, when an acid such as nitric is used to effect sample digestion in microwave units in open vessel(s), or sealed vessels equipment, there is the potential for the acid gas vapor released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a system with isolated and corrosion resistant safety devices prevents this from occurring.

4.2 Volumetric ware, volumetric flasks, and graduated cylinders, 50 and 100 mL capacity or equivalent.

4.3 Filter paper, qualitative or equivalent.

4.4 Filter funnel, polypropylene, polyethylene or equivalent.

4.5 Analytical balance, of appropriate capacity, with a ± 0.0001 g or appropriate precision for the weighing of the sample. Optionally, the vessel with sample and reagents may be weighed, with an appropriate precision balance, before and after microwave processing to evaluate the seal integrity in some vessel types.

5.0 REAGENTS

5.1 All reagents should be of appropriate purity or high purity (acids for example, should be sub-boiling distilled where possible) to minimize the blank levels due to elemental contamination. All references to water in the method refer to reagent water (Ref. 7). Other reagent grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Sec. 3.1.3 of this manual, for further information.

6.3 Refer to Chapter Three for the appropriate holding times and storage conditions.

7.0 PROCEDURE

7.1 Temperature control of closed vessel microwave instruments provides the main feedback control performance mechanism for the method. Control requires a temperature sensor in one or more vessels during the entire decomposition. The microwave decomposition system should sense the temperature to within ± 2.5 ^{o}C and permit adjustment of the microwave output power within 2 seconds.

7.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high concentration samples and low concentration samples, all digestion vessels (fluoropolymer liners only) should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80^{o}C, but less than boiling) for a minimum of two hours followed with hot (1:1) nitric acid (greater than 80^{o}C, but less than boiling) for a minimum of two hours and rinsed with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware (not used with HF) and storage containers should be cleaned by leaching with more dilute acids (approximately 10% V/V) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. To avoid precipitation of silver, ensure that all HCl has been rinsed from the vessels.

7.3 Sample Digestion

7.3.1 Weigh a well-mixed sample to the nearest 0.001 g into an appropriate vessel equipped with a pressure relief mechanism. For soils, ash, sediments, sludges, and siliceous wastes, initially use no more than 0.5 g. For oil or oil contaminated soils, initially use no more than 0.25 g.

7.3.2 Add 9 ± 0.1 mL concentrated nitric acid and 3 ± 0.1 mL concentrated hydrofluoric acid to the vessel in a fume hood. If the approximate silicon dioxide content of the sample is known, the quantity of hydrofluoric acid may be varied from 0 to 5 mL for stoichiometric reasons. Samples with higher concentrations of silicon dioxide (> 70%) may require higher concentrations of hydrofluoric acid (>3 mL HF). Alternatively samples with lower concentrations of silicon dioxide (< 10% to 0%) may require much less hydrofluoric acid (0.5 mL to 0 mL). Examples are presented in Table 1, 2, 3, and 6. Acid digestion reagent combinations used in the analysis of several matrices, listed in Table 7, provide guidance for the development of new matrix decomposition procedures.

7.3.3 The addition of other reagents with the original acids prior to digestion may permit more complete oxidation of organic sample constituents, address specific decomposition chemistry requirements, or address specific elemental stability and solubility problems.

The addition of 2 ± 2 mL concentrated hydrochloric acid to the nitric and hydrofluoric acids is appropriate for the stabilization of Ag, Ba, and Sb and high concentrations of Fe and Al in solution. The amount of HCl needed will vary depending on the matrix and the concentration of the analytes. The addition of hydrochloric acid may; however, limit the techniques or increase the difficulties of analysis. Examples are presented in Table 4.

The addition of hydrogen peroxide (30%) in small or catalytic quantities (such as 0.1 to 2 mL) may aid in the complete oxidation of organic matter.

The addition of water (double deionized) may (0 to 5 mL) improve the solubility of minerals and prevent temperature spikes due to exothermic reactions.

NOTE: Supporting documentation for the chemistry of this method has been prepared in chapters 2 and 3 of reference 3. It provides additional guidance and documentation of appropriate reagent, matrix and analyte combinations that can be employed in this method.

CAUTION: Only one acid mixture or quantity may be used in a single batch in the microwave to insure consistent reaction conditions between all vessels and monitored conditions. This limitation is due to the current practice of monitoring a representative vessel and applying a uniform microwave field to reproduce these reaction conditions within a group of vessels being simultaneously heated.

CAUTION: Toxic nitrogen oxide(s), hydrogen fluoride, and toxic chlorine (from the addition of hydrochloric acid) fumes are usually produced during digestion. Therefore, all steps involving open or the opening of microwave vessels must be performed in a properly operating fume ventilation system.

CAUTION: The analyst should wear protective gloves and face protection and must not at any time permit a solution containing hydrofluoric acid to come in contact with skin or lungs.

CAUTION: The addition of hydrochloric acid must be from concentrated hydrochloric acid and not from a premixed combination of acids as a buildup of toxic chlorine and possibly other gases will result from a premixed acid solution. This will over pressurize the vessel due to the release of these gases from solution upon heating. The gas effect is greatly lessened by following this suggestion.

CAUTION: When digesting samples containing volatile or easily oxidized organic compounds, initially weigh no more than 0.10 g and observe the reaction before capping the vessel. If a vigorous reaction occurs, allow the reaction to cease before capping the vessel. If no appreciable reaction occurs, a sample weight up to 0.25 g can be used.

CAUTION: The addition of hydrogen peroxide should only be done when the reactive components of the sample are known. Hydrogen peroxide may react rapidly and violently on easily oxidizable materials and should not be added if the sample may contain large quantities of easily oxidizable organic constituents.

7.3.4 The analyst should be aware of the potential for a vigorous reaction. If a vigorous reaction occurs upon the initial addition of reagent or the sample is suspected of containing easily oxidizable materials, allow the sample to predigest in the uncapped digestion vessel. Heat may be added in this step for safety considerations (for example the rapid release of carbon dioxide from carbonates, easily oxidized organic matter, etc.). Once the initial reaction has ceased, the sample may continue through the digestion procedure.

7.3.5 Seal the vessel according to the manufacturer's directions. Properly place the vessel in the microwave system according to the manufacturer's recommended specifications and connect appropriate temperature and pressure sensors to vessels according to manufacturer's specifications.

7.3.6 This method is a performance based method, designed to achieve or approach total decomposition of the sample through achieving specific reaction conditions. The temperature of each sample should rise to 180 ± 5 ºC in approximately 5.5 minutes and remain at 180 ± 5 ºC for 9.5 minutes. The temperature-time and pressure-time profile are given for a standard soil sample in Figure 1. The number of samples simultaneously digested is dependent on the analyst. The number may range from 1 to the maximum number of vessels that the microwave units magnetron can heat according to the manufacturer's or literature specifications (the number will depend on the power of the unit, the quantity and combination of reagents, and the heat loss from the vessels).

The pressure should peak between 5 and 15 minutes for most samples (Ref. 2, 3, 5). If the pressure exceeds the pressure limits of the vessel, the pressure will be reduced by the relief mechanism of the vessel.

The total decomposition of some components of a matrix may require or the reaction kinetics are dramatically improved with higher reaction temperatures. If microwave digestion systems and/or vessels are capable of achieving higher temperatures and pressures, the minimum digestion time of 9.5 minutes at a temperature of at least 180 ± 5°C is an appropriate

alternative. This change will permit the use of pressure systems if the analysis verifies that 180°C is the minimum temperature maintained by these control systems.

7.3.6.1 For reactive substances, the heating profile may be altered for safety purposes. The decomposition is primarily controlled by maintaining the reagents at 180 ± 5°C for 9.5 minutes, therefore the time it takes to heat the samples to 180 ± 5°C is not critical. The samples may be heated at a slower rate to prevent potential uncontrollable exothermic reactions. The time to reach 180 ± 5 ºC may be increased to 10 minutes provided that 180 ± 5 ºC is subsequently maintained for 9.5 minutes. Decomposition profiles are presented in Figures 1 and 2. The extreme difference in pressure is due to the gaseous digestion products.

7.3.6.2 Calibration control is applicable in reproducing this method provided the power in watts versus time parameters are determined to reproduce the specifications listed in 7.3.6. The calibration settings will be specific to the quantity and combination of reagents, quantity of vessels, and heat loss characteristics of the vessels (Ref 1). If calibration control is being used, any vessels containing acids for analytical blank purposes are counted as sample vessels and when fewer than the recommended number of samples are to be digested, the remaining vessels should be filled with the same acid mixture to achieve the full complement of vessels. This provides an energy balance, since the microwave power absorbed is proportional to the total absorbed mass in the cavity (Ref. 1). Irradiate each group of vessels using the predetermined calibration settings. (Different vessel types should not be mixed).

7.3.6.3 Pressure control for a specific matrix is applicable if instrument conditions are established using temperature control. Because each matrix will have a different reaction profile, performance using temperature control must be developed for every specific matrix type prior to use of the pressure control system.

7.3.7 At the end of the microwave program, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave system. When the vessels have cooled to near room temperature, determine if the microwave vessels have maintained a seal throughout the digestion. Due to the wide variability of vessel designs, a single procedure is not appropriate. For vessels that are sealed as discrete separate entities, the vessel weight may be taken before and after digestion to evaluate seal integrity. If the weight loss of sample exceeds 1% of the weight of the sample and reagents, then the sample is considered compromised. For vessels with burst disks, a careful visual inspection of the disk may identify compromised vessels. For vessels with resealing pressure relief mechanisms, an auditory or sometimes a physical sign indicates a vessel has vented.

7.3.8 Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Vent the vessels using the procedure recommended by the vessel manufacturer. Transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered.

7.3.8.1 Centrifugation: Centrifugation at 2,000 - 3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.3.8.2 Settling: If undissolved material remains such as TiO_2, or other refractory oxides, allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

7.3.8.3 Filtering: If necessary, the filtering apparatus must be thoroughly cleaned and prerinsed with dilute (approximately 10% V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned container.

7.3.9 If the hydrofluoric acid concentration is a consideration in the analysis technique such as with ICP methods, boric acid may be added to permit the complexation of fluoride to protect the quartz plasma torch. The amount of acid added may be varied, depending on the equipment and the analysis procedure. If this option is used, alterations in the measurement procedure to adjust for the boric acid and any bias it may cause are necessary. This addition will prevent the measurement of boron as one of the elemental constituents in the sample. Alternatively, a hydrofluoric acid resistant ICP torch may be used and the addition of boric acid would be unnecessary for this analytical configuration. All major manufacturers have hydrofluoric resistant components available for the analysis of solutions containing hydrofluoric acid.

CAUTION: The traditional use of concentrated solutions of boric acid can cause problems by turning the digestion solution cloudy or result in a high salt content solution interfering with some analysis techniques. Dilute solutions of boric acid or other methods of neutralization or reagent elimination are appropriate to avoid problems with HF and the glass sample introduction devices of analytical instrumentation. Gentle heating often serves to clear cloudy solutions. Matrix matching of samples and standards will eliminate viscosity differences.

7.3.10 The removal or reduction of the quantity of the hydrochloric and hydrofluoric acids prior to analysis may be desirable. The chemistry and volatility of the analytes of interest should be considered and evaluated when using this alternative. Evaporation to near dryness in a controlled environment with controlled pure gas and neutralizing and collection of exhaust interactions is an alternative where appropriate. This manipulation may be performed in the microwave system, if the system is capable of this function, or external to the microwave system in more common apparatus(s). This option must be tested and validated to determine analyte retention and loss and should be accompanied by equipment validation possibly using the standard addition method and standard reference materials. This alternative may be used to alter either the acid concentration and/or acid composition. Note: The final solution typically requires nitric acid to maintain appropriate sample solution acidity and stability of the elements. Commonly, a 2% (v/v) nitric acid concentration is desirable. Examples of analysis performed with and without removal of the hydrofluoric acid are presented in Table 5. Waste minimization techniques should be used to capture reagent

fumes. This procedure should be tested and validated in the apparatus and on standards before using on unknown samples.

7.3.11 Transfer or decant the sample into volumetric ware and dilute the digest to a known volume. The digest is now ready for analysis for elements of interest using appropriate elemental analysis techniques and/or SW-846 methods.

7.3.12 Sample size may be scaled-up from 0.1, 0.25, or 0.5 g to 1.0 g through a series of 0.2g sample size increments. Scale-up can produce different reaction conditions and/or produce increasing gaseous reaction products. Increases in sample size may not require alteration of the acid quantity or combination, but other reagents may be added to permit a more complete decomposition and oxidation of organic and other sample constituents where necessary (such as increasing the HF for the complete destruction of silicates). Each step of the scale-up must demonstrate safe operation before continuing.

7.4 Calculations: The concentrations determined are to be reported on the basis of the actual weight of the original sample.

7.5 Calibration of Microwave Equipment

NOTE: If the microwave unit uses temperature feedback control to follow performance specifications of the method, then the calibration procedure will not be necessary.

7.5.1 Calibration is the normalization and reproduction of a microwave field strength to permit reagent and energy coupling in a predictable and reproducible manner. It balances reagent heating and heat loss from the vessels and is equipment dependent due to the heat retention and loss characteristics of the specific vessel. Available power is evaluated to permit the microwave field output in watts to be transferred from one microwave system to another.

Use of calibration to control this reaction requires balancing output power, coupled energy, and heat loss to reproduce the temperature heating profile in section 7.3.6. The conditions for each acid mixture and each batch containing the same specified number of vessels must be determined individually. Only identical acid mixtures and vessel models and specified numbers of vessels may be used in a given batch.

7.5.2 For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the system. The calibration format required for laboratory microwave systems depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few systems have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (7.5.4), otherwise, the analyst must use the multiple point calibration method (7.5.3).

7.5.3 The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured; 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% using the procedure described in section 7.5.5. This data is clustered about the customary working power ranges. Nonlinearity has been encountered at the upper end of the calibration. If the system's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (±10 W), then the entire calibration should be reevaluated.

7.5.4 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using the procedure described in section 7.5.5. From the 2-point line calculate the power setting corresponding to the required power in watts specified in the procedure. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ±10 W, use the multiple point calibration in 7.5.3. This point should also be used to periodically verify the integrity of the calibration.

7.5.5 Equilibrate a large volume of water to room temperature (23 ± 2 ºC). One kg of reagent water is weighed (1,000.0 g ± 0.1 g) into a suitably inert polymeric beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be 23 ± 2 ºC measured to ± 0.05 ºC. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the system's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 30 seconds to ± 0.05 ºC. Use a new sample for each additional measurement. If the water is reused, both the water and the beaker must have returned to 23 ± 2 ºC. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship:

$$\text{Equation 1} \qquad P = \frac{K \; Cp \; m \; \Delta T}{t}$$

Where:

P = the apparent power absorbed by the sample in watts (W, W = joule sec^{-1})

K = the conversion factor for thermochemical calories_sec^{-1} to watts (which equals 4.184)

Cp = the heat capacity, thermal capacity, or specific heat (cal g^{-1} $ºC^{-1}$) of water

m = the mass of the water sample in grams (g)
ΔT = the final temperature minus the initial temperature (ºC)
t = the time in seconds (s)

Using the experimental conditions of 2 minutes and 1 kg of distilled water (heat capacity at 25 ºC is 0.9997 cal g^{-1} $ºC^{-1}$) the calibration equation simplifies to:

$$P = 34.86\ \Delta T$$

NOTE: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation should not vary by more than ±5 V. Electronic components in most microwave units are matched to the system's function and output. When any part of the high voltage circuit, power source, or control components in the system have been serviced or replaced, it will be necessary to recheck the system's calibration. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period determined by all involved parties based on program or project requirements. This method is restricted to use by, or under supervision of, experienced analysts. Refer to the appropriate section of Chapter One for additional quality control guidance.

8.2 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analytical process. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number. A duplicate sample should be prepared for each matrix type (i.e., soil, sludge, etc.).

8.3 Spiked samples and/or standard reference materials should be included with each group of samples processed or every 20 samples, whichever is the greater number. A spiked sample should also be included whenever a new sample matrix is being analyzed.

8.4 Blank samples should be prepared using the same reagents and quantities used in sample preparation, placed in vessels of the same type, and processed with the samples.

9.0 METHOD PERFORMANCE

9.1 Precision: Precision data for Method 3052 are presented in the tables of this method. Tables 1 through 6 provide a summary of total elemental analysis.

9.2 The performance criteria are provided as an example in Figure 1. The temperature profile will be within ± 5 ºC of the mean of the temperature profile, but the pressure curve will vary depending on the acid mixture and gaseous digestion products and the thermal insulating properties of the vessel. Figure 2 provides criteria for the digestion of an oil sample.

10.0 REFERENCES

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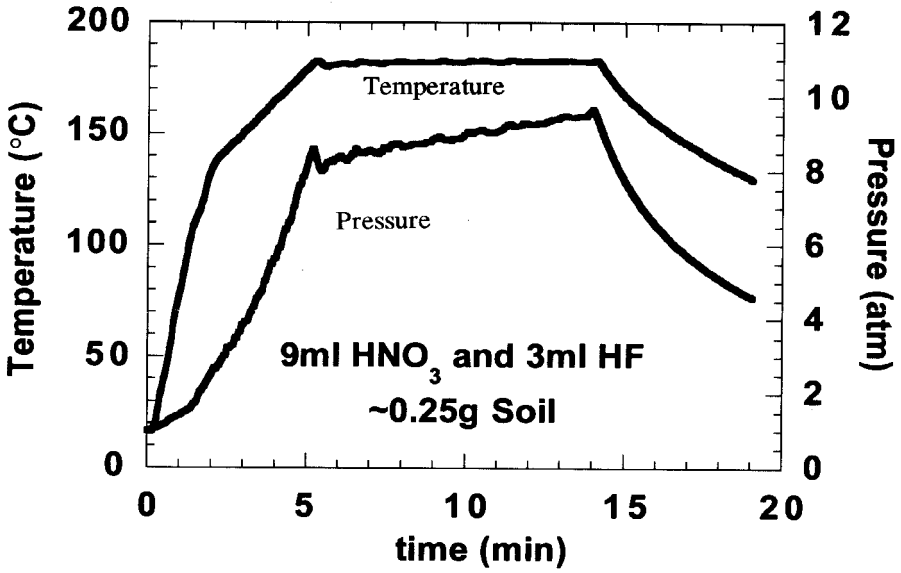


FIGURE 1. TYPICAL REACTION PROFILE FOR THE DIGESTION OF A SOIL (REF. 4 AND 8)

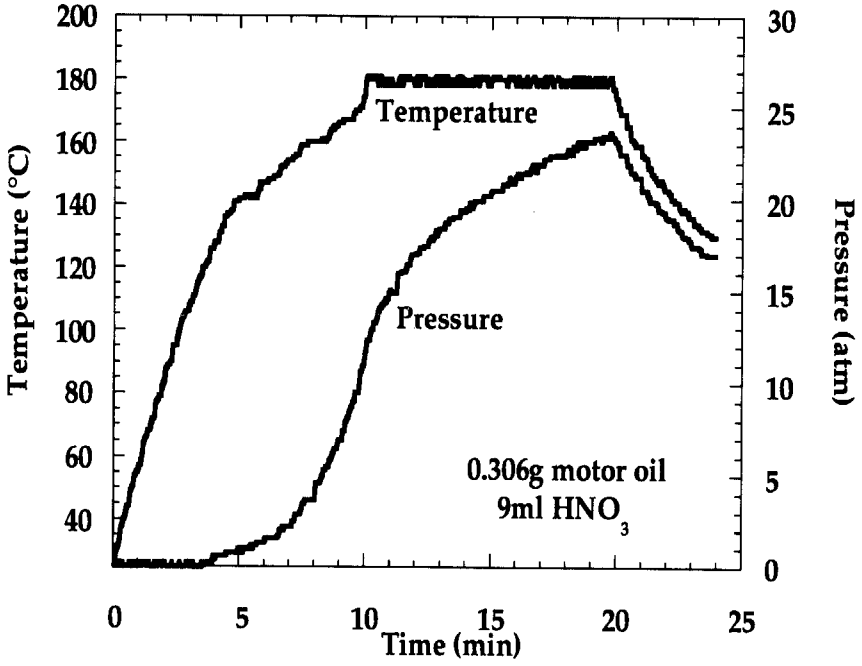


FIGURE 2. TYPICAL REACTION PROFILE FOR THE DIGESTION OF AN OIL (REF. 8)

TABLE 1
ANALYSIS OF NIST SRM 2704 (COMPILATION OF REFS. 2 AND 3)[a]
BUFFALO RIVER SEDIMENT

Element	Analyzed (µg/g)	Certified (µg/g)
Arsenic (n=4)	23.4 ± 2.6	23.4 ± 0.8
Cadmium (n=6)	3.5 ± 1.2	3.45 ± 0.22
Chromium (n=6)	132.9 ± 1.3	135 ± 5
Copper (n=6)	98.0 ± 4.2	98.6 ± 5.0
Lead (n=6)	155 ± 9.2	161 ± 17
Mercury (n=4)	1.49 ± 0.14	1.44 ± 0.07
Nickel (n=6)	43.6 ± 3.9	44.1 ± 3.0
Phosphorus (n=4)	1.016 ± 0.016 mg/g	0.998 ± 0.028 mg/g
Selenium (n=4)	1.13 ± 0.9	(1.1)
Sulfur (n=4)	3.56 ± 0.16	-----
Thallium (n=4)	1.15 ± 0.22	1.2 ± 0.2
Uranium (n=4)	2.97 ± 0.04	3.13 ± 0.13
Zinc (n=6)	441.9 ± 0.8	438 ± 12

[a] Digestion with 9 mL HNO_3 and 4 mL HF. Temperature and pressure conditions are as described in Section 7.3.6 of this method and similar to Figure 1. Data reported with 95% confidence intervals.

TABLE 2
ANALYSIS OF NIST SRM 2710 (REFS. 4 AND 3)[a]
MONTANA SOIL: HIGHLY ELEVATED TRACE ELEMENT CONCENTRATIONS (n=6)

Element	Analyzed (µg/g)	Certified (µg/g)
Antimony	39.3 ± 0.9 [b]	38.4 ± 3.0
Cadmium	21.9 ± 0.7 [a]	21.8 ± 0.2
Chromium	34.0 ± 3.2 [b]	(39)
Copper	2902 ± 83 [a]	2950 ± 130
Lead	5425 ± 251 [a]	5532 ± 80
Nickel	13.5 ± 1.0 [a]	14.3 ± 1.0
Silver	36.6 ± 0.5 [b]	35.3 ± 1.5
Zinc	7007 ± 111 [a]	6952 ± 91

[a] Digestion with either a. 9 mL HNO_3 and 4 mL HF or b. 9 mL HNO_3, 3 mL HF, & 2 mL HCl. Temperature and pressure conditions are as described in Sec. 7.3.6 of this method and similar to Figure 1. Data reported with 95% confidence intervals.

TABLE 3
NIST SRM 2711 (REFS. 4 AND 3)
MONTANA SOIL: MODERATELY ELEVATED TRACE ELEMENT CONCENTRATIONS (n=6)

Element	Analyzed (µg/g)	Certified (µg/g)
Cadmium	40.5 ± 1.0	41.70 ± 0.25
Chromium	45.5 ± 1.0	(47)
Copper	106.8 ± 3.4	114 ± 2
Lead	1161 ± 49	1162 ± 31
Nickel	19.6 ± 0.9	20.6 ± 1.1
Silver	4.3 ± 1.0	4.63 ± 0.39
Zinc	342 ± 9.4	350.4 ± 4.8

[a] Digestion with 9 mL HNO_3 and 4 mL HF. Temperature and pressure conditions are as described in Sec. 7.3.6 of this method and similar to Figure 1. Data reported with 95% confidence intervals.

TABLE 4
STABILIZATION AND RECOVERY OF ELEMENTS WITH HCl (REF. 3)[a] NIST SRM 2710
MONTANA SOIL: HIGHLY ELEVATED TRACE ELEMENT CONCENTRATIONS (n=6)

Element	HNO_3 & HF (µg/g)	HNO_3, HF & HCl (µg/g)	Certified (µg/g)
Antimony	33.1 ± 2.1	39.3 ± 0.9	38.4 ± 3.0
Silver	10.6 ± 4.5	36.6 ± 0.5	35.3 ± 1.5

[a] HNO_3 and HF - Digestion used 9 mL and 3 mL, respectively.
HNO_3, HF, and HCl - Digestion used 9 mL, 3 mL, and 2 mL respectively. Temperature and pressure conditions are as described in Sec. 7.3.6 of this method and similar to Figure 1. Data reported with 95% confidence intervals.

TABLE 5
FUMING OFF HYDROFLUORIC ACID WITH MICROWAVE EVAPORATION SYSTEM (REF 3)[a]
MONTANA SOIL: HIGHLY ELEVATED TRACE ELEMENT CONCENTRATIONS (n=4)

Element	Direct (µg/g)	Fumed (µg/g)	Certified (µg/g)
Antimony	39.3 ± 0.9	39.4 ± 0.9	38.4 ± 3.0
Cadmium	21.9 ± 0.7	23.3 ± 1.6	21.8 ± 0.2
Chromium	34.0 ± 3.2	32.4 ± 0.4	(39)
Copper	2902 ± 83	2870 ± 150	2950 ± 130
Lead	5425 ± 251	5502 ± 106	5532 ± 80
Nickel	13.5 ± 1.0	13.5 ± 0.8	14.3 ± 1.0
Silver	36.6 ± 0.5	38.9 ± 1.1	35.3 ± 1.5
Zinc	7007 ± 111	3992 ± 132	6952 ± 91

[a] Direct - Digestion used 9 mL HNO_3 and 3 mL HCl or 9 mL HNO_3, 3 mL HF, and 2 mL HCl
Fumed - Digestion used 9 mL HNO_3 and 3 mL HCl followed by the removal of the HF. Temperature and pressure conditions are as described in 7.3.6 of the method and similar to Figure 1. The digest solution was fumed in a microwave system under vacuum to ~1 mL and 3 mL HCl added. The digest solution was fumed to ~1 mL and 3 mL HNO_3 was added. The solution was fumed for a final step to ~1 mL and quantitatively transferred and diluted to final volume. Data reported with 95% confidence intervals.

TABLE 6
ANALYSIS OF NIST SRM 1084A (REF. 8) [a]
WEAR METALS IN OIL (100 ppm) (n=4)

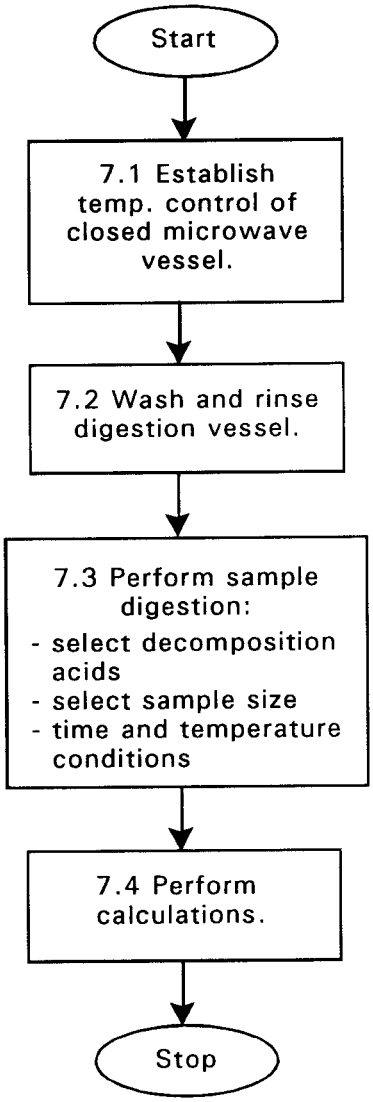
Element	Analyzed (µg/g)	Certified (µg/g)
Chromium	98.1 ± 1.1	98.3 ± 0.8
Copper	1.2.4 ± 2.4	100.0 ± 1.9
Lead	99.2 ± 2.3	101.1 ± 1.3
Nickel	99.2 ± 2.4	99.7 ± 1.6
Silver	102.7 ± 2.2	101.4 ± 1.5

[a] Digestion with 9 mL HNO_3 and 0.5 mL HF. Temperature and pressure conditions are as described in Sec. 7.3.6 of this method and similar to Figure 2. Data reported with 95% confidence intervals.

TABLE 7
DIGESTION PARAMETERS USED IN THE ANALYSIS OF SEVERAL MATRICES
BY METHOD 3052

Matrix	HNO_3	HF	HCl
Soil			
NIST SRM 2710 Highly Contaminated Montana Soil	9 mL	3 mL	0-2*mL
NIST SRM 2711 Moderately Contaminated Montana Soil	9	3	0-2*
Sediment			
NIST SRM 2704 Buffalo River Sediment	9	3	0-2*
Biological			
NIST SRM 1566a Oyster Tissue	9	0	0
NIST SRM 1577a Bovine Liver	9	0	0
Botanical			
NIST SRM 1515 Apple Leaves	9	0	0
NIST SRM 1547 Peach Leaves	9	0	0
NIST SRM 1572 Citrus Leaves	9	0.5	0
Waste Oil			
NIST SRM 1084a Wear-Metals in Lubricating Oil	9	0.5	0-2*

* HCl is added to stabilize elements such as Ag and Sb when they are analyzed.


Start
7.1 Establish temp. control of closed microwave vessel.
7.2 Wash and rinse digestion vessel.
7.3 Perform sample digestion:
- select decomposition acids
- select sample size
- time and temperature conditions
7.4 Perform calculations.
Stop

METHOD 6020

INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-µg/L concentrations of a large number of elements in water samples and in waste extracts or digests [1,2]. When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are required.

1.2 ICP-MS has been applied to the determination of over 60 elements in various matrices. Analytes for which EPA has demonstrated the acceptability of Method 6020 in a multi-laboratory study on solid wastes are listed in Table 1. Acceptability of the method for an element was based upon the multi-laboratory performance compared with that of either furnace atomic absorption spectroscopy or inductively coupled plasma-atomic emission spectroscopy. It should be noted that the multi-laboratory study was conducted in 1986. Multi-laboratory performance data for the listed elements (and others) are provided in Section 9. Instrument detection limits, sensitivities, and linear ranges will vary with the matrices, instrumentation, and operating conditions. In relatively simple matrices, detection limits will generally be below 0.02 µg/L.

1.3 If Method 6020 is used to determine any analyte not listed in Table 1, it is the responsibility of the analyst to demonstrate the accuracy and precision of the Method in the waste to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality (see Section 8.4).

1.4 Use of this method is restricted to spectroscopists who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS.

1.5 An appropriate internal standard is required for each analyte determined by ICP-MS. Recommended internal standards are ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho,and ^{209}Bi. The lithium internal standard should have an enriched abundance of ^{6}Li, so that interference from lithium native to the sample is minimized. Other elements may need to be used as internal standards when samples contain significant amounts of the recommended internal standards.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples which require total ("acid-leachable") values must be digested using appropriate sample preparation methods (such as Methods 3005 - 3051).

2.2 Method 6020 describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

3.0 INTERFERENCES

3.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isoptope, or use of another method.

3.2 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature [3,4]. Examples include $ArCl^+$ ions on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature [5], the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting statistics. Because the ^{35}Cl natural abundance of 75.77 percent is 3.13 times the ^{37}Cl abundance of 24.23 percent, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06 percent of the $^{40}Ar^{35}Cl^+$ signal):

> corrected arsenic signal (using natural isotopes abundances for coefficient approximations) =
>
> (m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal),
> (where the final term adjusts for any selenium contribution at 77 m/z),
>
> NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, (e.g., $^{81}BrH^+$ from bromine wastes [6]).

Similarly,

corrected cadmium signal (using natural isotopes abundances for coefficient approximations) =

(m/z 114 signal) - (0.027)(m/z 118 signal) - (1.63)(m/z 108 signal), (where last 2 terms adjust for any tin or MoO^+ contributions at m/z 114).

NOTE: Cadmium values will be biased low by this type of equation when $^{92}ZrO^+$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{94}ZrOH^+$) and indirect ($^{90}ZrO^+$) additive interferences when Zr is present.

NOTE: As for the arsenic equation above, the coefficients in the Cd equation are **ONLY** illustrative. The most appropriate coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting precision.

The accuracy of these types of equations is based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found [7] to be reliable, e.g., oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferant. This type of correction has been reported [7] for oxide-ion corrections using ThO^+/Th^+ for the determination of rare earth elements. The use of aerosol desolvation and/or mixed plasmas have been shown to greatly reduce molecular interferences [8]. These techniques can be used provided that method detection limits, accuracy, and precision requirements for analysis of the samples can be met.

3.3 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement [9]. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been currently recommended [10] to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes [11]. When the intensity level of an internal standard is less than 30 percent or greater than 120 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed after a fivefold (1+4) or greater dilution has been performed.

3.4 Memory interferences can occur when there are large concentration differences between samples or standards which are analyzed sequentially. Sample

deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences which are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled plasma-mass spectrometer:

4.1.1 A system capable of providing resolution, better than or equal to amu at 10% peak height is required. The system must have a mass range from at least 6 to 240 amu and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution are recommended.

4.1.2 Argon gas supply: high-purity grade (99.99%).

5.0 REAGENTS

5.1 Acids used in the preparation of standards and for sample processing must be of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at less than 2 per cent (v/v) is required for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed on the analytes when hydrochloric and sulfuric acids are used [3,4]. Concentrations of antimony and silver between 50-500 µg/L require 1% (v/v) HCl for stability; for concentrations above 500 µg/L Ag, additional HCl will be needed.

5.2 Reagent water: All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 or greater purity). See Method 6010A, Section 5.3, for instructions on preparing standard solutions from solids.

5.3.1 Bismuth internal standard solution, stock, 1 mL = 100 µg Bi: Dissolve 0.1115 g Bi_2O_3 in a minimum amount of dilute HNO_3 . Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.2 Holmium internal standard solution, stock, 1 mL = 100 µg Ho: Dissolve 0.1757 g $Ho_2(CO_3)_2{\cdot}5H_2O$ in 10 mL reagent water and 10 mL HNO_3. After dissolution is complete, warm the solution to d egas. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.3 Indium internal standard solution, stock, 1 mL = 100 µg In: Dissolve 0.1000 g indium metal in 10 mL conc. HNO_3. Dilute to 1,000 mL with reagent water.

5.3.4 Lithium internal standard solution, stock, 1 mL = 100 µg ^6Li: Dissolve 0.6312 g 95-atom-% ^6Li, Li_2CO_3 in 10 mL of reagent water and 10 mL HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.5 Rhodium internal standard solution, stock, 1 mL = 100 µg Rh: Dissolve 0.3593 g ammonium hexachlororhodate (III) $(NH_4)_3RhCl_6$ in 10 mL reagent water. Add 100 mL conc. HCl and dilute to 1,000 mL with reagent water.

5.3.6 Scandium internal standard solution, stock, 1 mL = 100 µg Sc: Dissolve 0.15343 g Sc_2O_3 in 10 mL (1+1) hot HNO_3. Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.7 Terbium internal standard solution, stock, 1 mL = 100 µg Tb: Dissolve 0.1828 g $Tb_2(CO_3)_3 \cdot 5H_2O$ in 10 mL (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.8 Yttrium internal standard solution, stock, 1 mL = 100 µg Y: Dissolve 0.2316 g $Y_2(CO_3)_3 \cdot 3H_2O$ in 10 mL (1+1) HNO_3. Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.9 Titanium solution, stock, 1 mL = 100 µg Ti: Dissolve 0.4133 g $(NH_4)_2TiF_6$ in reagent water. Add 2 drops conc. HF and dilute to 1,000 mL with reagent water.

5.3.10 Molybdenum solution, stock, 1 mL = 100 µg Mo: Dissolve 0.2043 g $(NH_4)_2MoO_4$ in reagent water. Dilute to 1,000 mL with reagent water.

5.4 Mixed calibration standard solutions are prepared by diluting the stock-standard solutions to levels in the linear range for the instrument in a solvent consisting of 1 percent (v/v) HNO_3 in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. Internal standards may be added on-line at the time of analysis using a second channel of the peristaltic pump and an appropriate mixing manifold.) Generally, an internal standard should be no more than 50 amu removed from the analyte. Recommended internal standards include ^6Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{169}Ho, and ^{209}Bi. Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon bottles for storage. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control standard (see Section 5.7) and monitored weekly for stability.

5.5 Blanks: Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The preparation blank is used to monitor for possible contamination resulting from

the sample preparation procedure. The rinse blank is used to flush the system between all samples and standards.

5.5.1 The calibration blank consists of the same concentration(s) of the same acid(s) used to prepare the final dilution of the calibrating solutions of the analytes [often 1 percent HNO_3 (v/v) in reagent water] along with the selected concentrations of internal standards such that there is an appropriate internal standard element for each of the analytes. Use of HCl for antimony and silver is cited in Section 5.1

5.5.2 The preparation (or reagent) blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.

5.5.3 The rinse blank consists of 1 to 2 percent HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples.

NOTE: The ICS solutions in Table 2 are intended to evaluate corrections for known interferences on only the analytes in Table 1. If Method 6020 is used to determine an element not listed in Table 1, it is the responsibility of the analyst to modify the ICS solutions, or prepare an alternative ICS solution, to allow adequate verification of correction of interferences on the unlisted element (see section 8.4).

5.6 The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^{+}$ on $^{51}V^{+}$ and $^{40}Ar^{35}Cl^{+}$ on $^{75}As^{+}$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

5.6.1 These solutions must be prepared from ultra-pure reagents. They can be obtained commercially or prepared by the following procedure.

5.6.1.1 Mixed ICS solution I may be prepared by adding 13.903 g $Al(NO_3)_3{\cdot}9H_2O$, 2.498 g $CaCO_3$ (dried at 180 C for 1 h before weighing), 1.000 g Fe, 1.658 g MgO, 2.305 g Na_2CO_3, and 1.767 g K_2CO_3 to 25 mL of reagent water. Slowly add 40 mL of (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Cool and dilute to 1,000 mL with reagent water.

5.6.1.2 Mixed ICS solution II may be prepared by slowly adding 7.444 g 85 % H_3PO_4, 6.373 g 96% H_2SO_4, 40.024 g 37% HCl, and 10.664 g citric acid $C_6O_7H_8$ to 100 mL of reagent water. Dilute to 1,000 mL with reagent water.

5.6.1.3 Mixed ICS solution III may be prepared by adding 1.00 mL each of 100-µg/mL arsenic, cadmium, chromium, cobalt, copper, manganese, nickel, silver, and zinc stock solutions to about

50 mL reagent water. Add 2.0 mL concentrated HNO_3, and dilute to 100.0 mL with reagent water.

5.6.1.4 Working ICS Solutions

5.6.1.4.1 ICS-A may be prepared by adding 10.0 mL of mixed ICS solution I (5.7.1.1), 2.0 mL each of 100-µg/mL titanium stock solution (5.3.9) and molybdenum stock solution (5.3.10), and 5.0 mL of mixed ICS solution II (5.7.1.2). Dilute to 100 mL with reagent water. ICS solution A must be prepared fresh weekly.

5.6.1.4.2 ICS-AB may be prepared by adding 10.0 mL of mixed ICS solution I (5.7.1.1), 2.0 mL each of 100-µg/mL titanium stock solution (5.3.9) and molybdenum stock solution (5.3.10), 5.0 mL of mixed ICS solution II (5.7.1.2), and 2.0 mL of Mixed ICS solution III (5.7.1.3). Dilute to 100 mL with reagent water. Although the ICS solution AB must be prepared fresh weekly, the analyst should be aware that the solution may precipitate silver more quickly.

5.7 The quality control standard is the initial calibration verification solution (ICV), which must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard is defined as a standard composed of the analytes from a source different from those used in the standards for instrument calibration.

5.8 Mass spectrometer tuning solution. A solution containing elements representing all of the mass regions of interest (for example, 10 µg/L of Li, Co, In, and Tl) must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications (see Section 7.5). This solution is also used to verify that the instrument has reached thermal stability (See Section 7.4).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Sample collection procedures should address the considerations described in Chapter Nine of this Manual.

6.2 See the introductory material in Chapter Three, Inorganic Analytes, Sections 3.1.3 for information on sample handling and preservation. Only polyethylene or fluorocarbon (TFE or PFA) containers are recommended for use in Method 6020.

7.0 PROCEDURE

7.1 Solubilization and digestion procedures are presented in the Sample Preparation Methods (e.g., Methods 3005 - 3051).

7.2 Initiate appropriate operating configuration of the instruments computer according to the instrument manufacturer's instructions.

7.3 Set up the instrument with the proper operating parameters according to the instrument manufacturer's instructions.

7.4 Operating conditions: The analyst should follow the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. This must be verified by analyzing a tuning solution (Section 5.8) at least four times with relative standard deviations of $\leq$ 5% for the analytes contained in the tuning solution.

> NOTE: Precautions must be taken to protect the channel electron multiplier from high ion currents. The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.

7.5 Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less than 0.9 amu full width at 10 percent peak height.

7.6 Calibrate the instrument for the analytes of interest (recommended isotopes for the analytes in Table 1 are provided in Table 3), using the calibration blank and at least a single initial calibration standard according to the instrument manufacturer's procedure. Flush the system with the rinse blank (5.5.3) between each standard solution. Use the average of at leastthree integrations for both calibration and sample analyses.

7.7 All masses which could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks. The recommended isotopes to be monitored are liste in Table 3.

7.8 Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the calibration verification solution (Section 5.7). When measurements exceed ± 10% of the accepted value, the analyses must be terminated, the problem corrected, the instrument recalibrated, and the new calibration verified. Any samples analyzed under an out-of-control calibration must be reanalyzed. During the course of an analytical run, the instrument may be "resloped" or recalibrated to correct for instrument drift. A recalibration must then be followed immediately by a new analysis of a CCV and CCB before any further samples may be analyzed.

7.9 Flush the system with the rinse blank solution (5.5.3) until the signal levels return to the method's levels of quantitation (usually about 30 seconds) before the analysis of each sample (see Section 7.7). Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data. Analyze the calibration verification solution (Section 5.6) and the calibration blank (Section 5.5.1) at a frequency of at least once every 10 analytical samples. Flow-injection systems may be used as long as they can meet the performance criteria of this method.

7.10 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte (or species needed for a correction) or measure an alternate less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (see Sec. 7.6 and 7.8).

7.11 Calculations: The quantitative values shall be reported in appropriate units, such as micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values.

7.11.1 If appropriate, or required, calculate results for solids on a dry-weight basis as follows:

(1) A separate determination of percent solids must be performed.

(2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry weight)(mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

C = Digest Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample

$$S = \frac{\%\ \text{Solids}}{100}$$

Calculations should include appropriate interference corrections (see Section 3.2 for examples), internal-standard normalization, and the summation of signals at 206, 207, and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and be available for easy reference or inspection.

8.2 Instrument Detection Limits (IDLs) in µg/L can be estimated by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs must be determined at least every three months and kept with the instrument log book. Refer to Chapter One for additional guidance.

8.3 The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall between 30 and 120 percent of the intensity of that internal standard in the initial calibration standard, the following procedure is followed. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal-standard intensities fall within the prescribed window. The intensity levels of the internal standards for the calibration blank (Section 5.5.1) and instrument check standard (Section 5.6) must agree within ± 20 percent of the intensity level of the internal standard of the original calibration solution. If they do not agree, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

8.4 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantification and the concentration of interferents are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferant itself, but that a molecular species may be monitored to indicate the presence of the interferent. When correcttion equations are used, all QC criteria must also be met. Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element or molecular-ion cluster provide information useful for quality assurance.

NOTE: Only isobaric elemental, molecular, and doubly charged interference corrections which use the observed isotopic-response ratios or parent-to-oxide ratios (provided an oxide internal standard is used as described in Section 3.2) for each instrument system are acceptable corrections for use in Method 6020.

8.5 Dilution Test: If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the reagent blank, refer to Section 5.5.2), an analysis of a fivefold (1+4) dilution must agree within ± 10% of the original determination. If not, an interference effect must be suspected. One dilution test must be included for each twenty samples (or less) of each matrix in a batch.

8.6 Post-Digestion Spike Addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 percent of the known value or within the laboratory derived acceptance criteria. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and reanalyzed to compensate for the matrix effect. Results must agree to within 10% of the original determination. The use of a standard-addition analysis procedure may also be used to compensate for this effect (Refer to Method 7000).

8.7 A Laboratory Control Sample (LCS) should be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the test samples. One LCS should be prepared and analyzed for each sample batch at a frequency of one LCS for each 20 samples or less.

8.8 Check the instrument calibration by analyzing appropriate quality control solutions as follows:

8.8.1 Check instrument calibration using a calibration blank (Section 5.5.1) and the initial calibration verification solution (Sections 5.7 and 7.9).

8.8.2 Verify calibration at a frequency of every 10 analytical samples with the instrument check standard (Section 5.6) and the calibration blank (Section 5.5.1). These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last sample.

8.8.3 The results of the initial calibration verification solution and the instrument check standard must agree within ± 10% of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument. Any sample analyzed under an out-of-control calibration must be reanalyzed .

8.8.4 The results of the calibration blank must be less than 3 times the current IDL for each element. If this is not the case, the reason for the out-of-control condition must be found and corrected, and affected samples must be reanalyzed. If the laboratory consistently has concentrations greater than 3 times the IDL, the IDL may be indicative of an estimated IDL and should be re-evaluated.

8.9 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. Do this by analyzing the interference check solutions A and AB. The analyst should be aware that precipitation from solution AB may occur with some elements, specifically silver. Refer to Section 3.0 for a discussion on intereferences and potential solutions to those intereferences if additional guidance is needed.

8.10 Analyze one duplicate sample for every matrix in a batch at a frequency of one matrix duplicate for every 20 samples.

8.10.1 The relative percent difference (RPD) between duplicate determinations must be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (duplicate)

A control limit of 20% RPD should not be exceeded for analyte values greater than 100 times the instrumental detection limit. If this limit is exceeded, the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition must be reanalyzed.

9.0 METHOD PERFORMANCE

9.1 In an EPA multi-laboratory study, 10 laboratories applied the ICP-MS technique to both aqueous and solid samples. TABLE 4 summarizes the method performance data for aqueous samples. Performance data for solid samples is provided in TABLE 5.

10.0 REFERENCES

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TABLE 1. ELEMENTS APPROVED FOR ICP-MS DETERMINATION

Element	CAS* #
Aluminum	7429-90-5
Antimony	7440-36-0
Arsenic	7440-38-2
Barium	7440-39-3
Beryllium	7440-41-7
Cadmium	7440-43-9
Chromium	7440-47-3
Cobalt	7440-48-4
Copper	7440-50-8
Lead	7439-92-1
Manganese	7439-96-5
Nickel	7440-02-0
Silver	7440-22-4
Thallium	7440-28-0
Zinc	7440-66-6

TABLE 2. RECOMMENDED INTERFERENCE CHECK SAMPLE COMPONENTS AND CONCENTRATIONS

Solution component	Solution A Concentration(mg/L)	Solution AB Concentration (mg/L)
Al	100.0	100.0
Ca	100.0	100.0
Fe	100.0	100.0
Mg	100.0	100.0
Na	100.0	100.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	1000.0	1000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.0200
Cd	0.0	0.0200
Cr	0.0	0.0200
Co	0.0	0.0200
Cu	0.0	0.0200
Mn	0.0	0.0200
Ni	0.0	0.0200
Ag	0.0	0.0200
Zn	0.0	0.0200

TABLE 3. RECOMMENDED ISOTOPES FOR SELECTED ELEMENTS

Mass	Element of interest
27	Aluminum
121, **123**	Antimony
75	Arsenic
138, 137, 136, **135**, 134	Barium
9	Beryllium
209	Bismuth (IS)
114, 112, **111**, 110, 113, 116, 106	Cadmium
42, 43, **44**, 46, 48	Calcium (I)
35, 37, (77, 82)[a]	Chlorine (I)
52, **53**, **50**, 54	Chromium
59	Cobalt
63, **65**	Copper
165	Holmium (IS)
115, 113	Indium (IS)
56, **54**, **57**, 58	Iron (I)
139	Lanthanum (I)
208, **207**, **206**, 204	Lead
6[b], 7	Lithium (IS)
24, **25**, **26**	Magnesium (I)
55	Manganese
98, 96, 92, **97**, 94, (108)[a]	Molybdenum (I)
58, **60**, 62, **61**, 64	Nickel
39	Potassium (I)
103	Rhodium (IS)
45	Scandium (IS)
107, **109**	Silver
23	Sodium (I)
159	Terbium (IS)
205, 203	Thallium
120, **118**	Tin (I)
89	Yttrium (IS)
64, **66**, **68**, **67**, 70	Zinc

NOTE: Method 6020 is recommended for only those analytes listed in Table 1. Other elements are included in this table because they are potential interferents (labeled I) in the determination of recommended analytes, or because they are commonly used internal standards (labeled IS). Isotopes are listed in descending order of natural abundance. The most generally useful isotopes are underlined and in boldface, although certain matrices may require the use of alternative isotopes. [a] These masses are also useful for interference correction (Section 3.2). [b] Internal standard must be enriched in the ^{6}Li isotope. This minimizes interference from indigenous lithium.

TABLE 4. ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR AQUEOUS SOLUTIONS

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	95 - 100	11 - 14	14 - 14	4
Antimony	d	5.0 - 7.6	16 - 16	3
Arsenic	97 - 114	7.1 - 48	12 - 14	4
Barium	91 - 99	4.3 - 9.0	16 - 16	5
Beryllium	103 - 107	8.6 - 14	13 - 14	3
Cadmium	98 - 102	4.6 - 7.2	18 - 20	3
Calcium	99 - 107	5.7 - 23	17 - 18	5
Chromium	95 - 105	13 - 27	16 - 18	4
Cobalt	101 - 104	8.2 - 8.5	18 - 18	3
Copper	85 - 101	6.1 - 27	17 - 18	5
Iron	91 - 900	11 - 150	10 - 12	5
Lead	71 - 137	11 - 23	17 - 18	6
Magnesium	98 - 102	10 - 15	16 - 16	5
Manganese	95 - 101	8.8 - 15	18 - 18	4
Nickel	98 - 101	6.1 - 6.7	18 - 18	2
Potassium	101 - 114	9.9 - 19	11 - 12	5
Selenium	102 - 107	15 - 25	12 - 12	3
Silver	104 - 105	5.2 - 7.7	13 - 16	2
Sodium	82 - 104	24 - 43	9 - 10	5
Thallium	88 - 97	9.7 - 12	18 - 18	3
Vanadium	107 - 142	23 - 68	8 - 13	3
Zinc	93 - 102	6.8 - 17	16 - 18	5

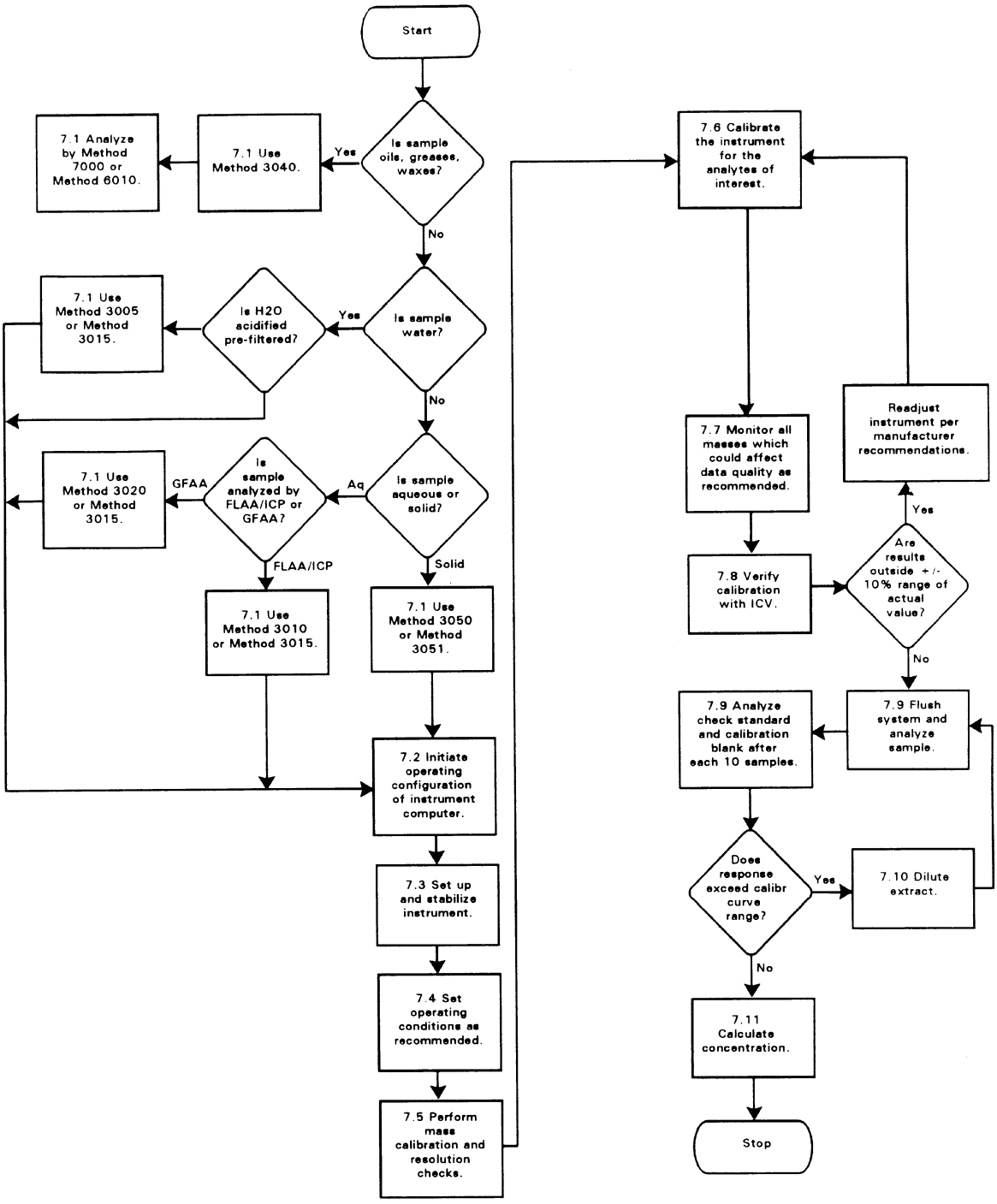
[a] Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique. [b] N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value). [c] S is the number of samples with results greater than the limit of quantitation. [d] No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

TABLE 5. ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR SOLID MATRICES

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	83 - 101	11 - 39	13 - 14	7
Antimony	d	12 - 21	15 - 16	2
Arsenic	79 - 102	12 - 23	16 - 16	7
Barium	100 - 102	4.3 - 17	15 - 16	7
Beryllium	50 - 87	19 - 34	12 - 14	5
Cadmium	93 - 100	6.2 - 25	19 - 20	5
Calcium	95 - 109	4.1 - 27	15 - 17	7
Chromium	77 - 98	11 - 32	17 - 18	7
Cobalt	43 - 102	15 - 30	17 - 18	6
Copper	90 - 109	9.0 - 25	18 - 18	7
Iron	87 - 99	6.7 - 21	12 - 12	7
Lead	90 - 104	5.9 - 28	15 - 18	7
Magnesium	89 - 111	7.6 - 37	15 - 16	7
Manganese	80 - 108	11 - 40	16 - 18	7
Nickel	87 - 117	9.2 - 29	16 - 18	7
Potassium	97 - 137	11 - 62	10 - 12	5
Selenium	81	39	12	1
Silver	43 - 112	12 - 33	15 - 15	3
Sodium	100 - 146	14 - 77	8 - 10	5
Thallium	91	33	18	1
Vanadium	83 - 147	20 - 70	6 - 14	7
Zinc	84 - 124	14 - 42	18 - 18	7

[a] Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique. [b] N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value). [c] S is the number of samples with results greater than the limit of quantitation. [d] No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

METHOD 6020
INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY



METHOD 7742

SELENIUM (ATOMIC ABSORPTION, BOROHYDRIDE REDUCTION)

1.0 SCOPE AND APPLICATION

1.1 Method 7742 is an atomic absorption procedure for determining 3 µg/L to 750 µg/L concentrations of selenium in wastes, mobility procedure extracts, soils, and ground water. Method 7742 is approved for sample matrices that contain a total of up to 1000 mg/L concentrations of cobalt, copper, iron, mercury, and nickel. A solid sample can contain up to 10% by weight of the interferents before exceeding 1000 mg/L in a digested sample. All samples including aqueous matrices must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine the applicability of the method to a given waste.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric acid digestion procedure described in Method 3010 for aqueous and extract samples and the nitric/peroxide/hydrochloric acid digestion procedure described in Method 3050 (furnace AA option) for sediments, soils, and sludges. Excess peroxide is removed by evaporating samples to near-dryness at the end of the digestion followed by dilution to volume and degassing the samples upon addition of urea. The selenium is converted to the +4 oxidation state during digestion in HCl. After a 1:10 dilution, selenium is then converted to its volatile hydride using hydrogen produced from the reaction of the acidified sample with sodium borohydride in a continuous-flow hydride generator.

2.2 The volatile hydrides are swept into, and decompose in, a heated quartz absorption cell located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the selenium concentration.

2.3 The typical detection limit for this method is 3 µg/L.

3.0 INTERFERENCES

3.1 Very high (>1000 mg/L) concentrations of cobalt, copper, iron, mercury, and, nickel can cause analytical interferences through precipitation as reduced metals and associated blockage of transfer lines and fittings.

3.2 Traces of peroxides left following the sample work-up can result in analytical interferences. Peroxides must be removed by evaporating each sample to near-dryness followed by reacting each sample with urea and allowing sufficient time for degassing before analysis (see Sections 7.1 and 7.2).

3.3 Even after acid digestion, flame gases and organic compounds may remain in the sample. Flame gases and organic compounds can absorb at the analytical wavelengths and background correction should be used.

4.0 APPARATUS AND MATERIALS

4.1 Electric hot plate: Large enough to hold at least several 100 mL Pyrex digestion beakers.

4.2 A continuous-flow hydride generator: A commercially available continuous-flow sodium borohydride/HCl hydride generator or a generator constructed similarly to that shown in Figure 1 (P. S. Analytical or equivalent).

4.2.1 Peristaltic Pump: A four-channel, variable-speed peristaltic pump to permit regulation of liquid-stream flow rates (Ismatec Reglo-100 or equivalent). Pump speed and tubing diameters should be adjusted to provide the following flow rates: sample/blank flow = 4.2 mL/min; borohydride flow = 2.1 mL/min.

4.2.2 Sampling Valve (optional): A sampling valve (found in the P. S. Analytical Hydride Generation System or equivalent) that allows switching between samples and blanks (rinse solution) without introduction of air into the system will provide more signal stability.

4.2.3 Transfer Tubing and Connectors: Transfer tubing (1 mm I.D.), mixing T's, and connectors are made of fluorocarbon (PFA or TFM) and are of compatible sizes to form tight, leak-proof connections (Latchat, Technicon, etc. flow injection apparatus accessories or equivalent).

4.2.4 Mixing Coil: A 20-turn coil made by wrapping transfer tubing around a 1-cm diameter by 5-cm long plastic or glass rod (see Figure 1).

4.2.5 Mixing Coil Heater, if appropriate: A 250-mL Erlenmeyer flask containing 100 mL of water heated to boiling on a dedicated one-beaker hotplate (Corning PC-35 or equivalent). The mixing coil in 4.2.4 is immersed in the boiling water to speed kinetics of the hydride forming reactions and increase solubility of interfering reduced metal precipitates.

4.2.6 Gas-Liquid Separator: A glass apparatus for collecting and separating liquid and gaseous products (P. S. Analytical accessory or equivalent) which allows the liquid fraction to drain to waste and gaseous products above the liquid to be swept by a regulated carrier gas (argon) out of the cell for analysis. To avoid undue carrier gas dilution, the gas volume above the liquid should not exceed 20 mL. See Figure 1 for an acceptable separator shape.

4.2.7 Condensor: Moisture picked up by the carrier gas must be removed before encountering the hot absorbance cell. The moist carrier gas with the hydrides is dried by passing the gasses through a small (< 25

mL) volume condensor coil (Ace Glass Model 6020-02 or equivalent) that is cooled to 5°C by a water chiller (Neslab RTE-110 or equivalent). Cool tap-water in place of a chiller is acceptable.

4.2.8 Flow Meter/Regulator: A meter capable of regulating up to 1 L/min of argon carrier gas is recommended.

4.3 Absorbance Cell: A 17-cm or longer quartz tube T-cell (windowless is strongly suggested) is recommended, as shown in Figure 1 (Varian Model VGA-76 accessory or equivalent). The cell is held in place by a holder that positions the cell about 1 cm over a conventional AA air-acetylene burner head. In operation, the cell is heated to around 900°C.

4.4 Atomic absorption spectrophotometer: Single- or dual- channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with an appropriate recording device.

4.5 Burner: As recommended by the particular instrument manufacturer for an air-acetylene flame. An appropriate mounting bracket attached to the burner that suspends the quartz absorbance cell between 1 and 2 cm above the burner slot is required.

4.6 Selenium hollow cathode lamp or selenium electrodeless discharge lamp and power supply. Super-charged hollow-cathode lamps or EDL lamps are recommended for maximum sensitivity.

4.7 Strip-chart recorder (optional): Connect to output of spectrophotometer.

5.0 REAGENTS

5.1 Reagent water : Water must be monitored for impurities. Refer to Chapter 1 for definition of Reagent water.

5.2 Concentrated nitric acid (HNO_3): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.3 30% Hydrogen peroxide (H_2O_2): Peroxide must be a tin-free grade.

5.4 Concentrated hydrochloric acid (HCl): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.5 Diluent solution: A 3% HCl solution in reagent water must be prepared as a diluent solution if excessive levels of analytes or interfering metals are found in the undiluted samples.

5.6 Urea (H_2NCONH_2): A 5.00-g portion of reagent grade urea must be added to a 25-mL aliquot of each sample for removal of excess peroxide through degassing (see Section 7.2).

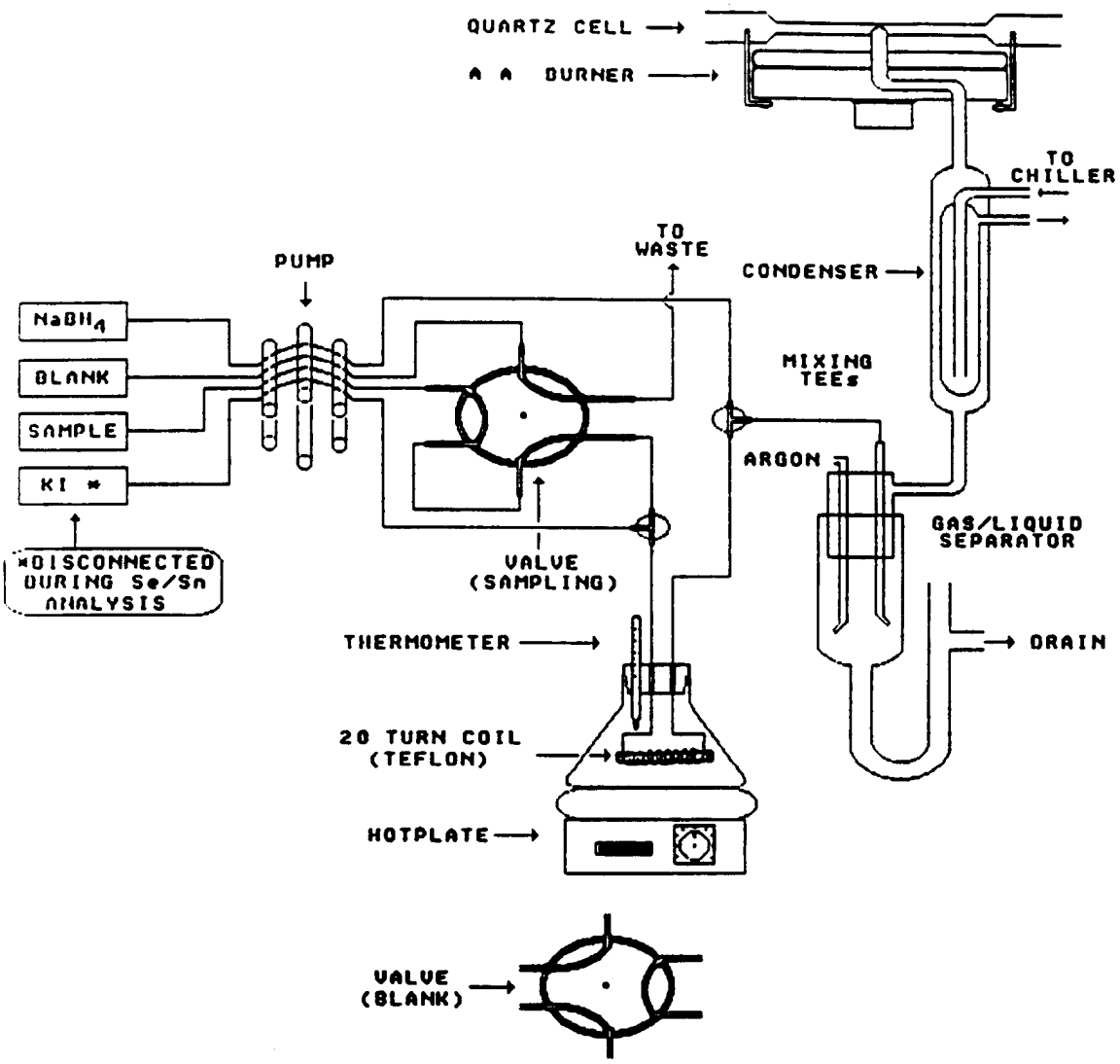


Figure 1. Continuous-flow sodium borohydride/hydride generator apparatus setup and an AAS sample introduction system

5.7 4% Sodium Borohydride ($NaBH_4$): A 4 % sodium borohydride solution (20 g reagent-grade $NaBH_4$ plus 2 g sodium hydroxide dissolved in 500 mL of reagent water) must be prepared for conversion of the selenium to its hydride.

5.8 Selenium solutions:

5.8.1 **Selenium standard stock solution** (1,000 mg/L): Either procure certified aqueous standards from a supplier and verify by comparison with a second standard, or dissolve 0.3453 g of selenious acid (assay 96.6% of H_2SeO_3) in 200 mL of reagent water (1 mL = 1 mg Se).

5.8.2 **Selenium working stock solution:** Pipet 1 mL selenium standard stock solution into a 1 L volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated HNO_3/liter. The concentration of this solution is 1 mg Se/L (1 mL = 1 µg Se).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are suspected to be present in the samples.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Place a 100-mL portion of an aqueous sample or extract or 1.000 g of a dried solid sample in a 250-mL digestion beaker. Digest aqueous samples and extracts according to Method 3010. Digest solid samples according to Method 3050 (furnace AA option) with the following modifications: add 5 mL of concentrated hydrochloric acid just prior to the final volume reduction stage to aid in conversion of selenium to its plus four state; the final volume reduction should be to less than 5 mL but not to dryness to adequately remove excess hydrogen peroxide (see note). After dilution to volume, further dilution with diluent may be necessary if the analyte is known to exceed 750 µg/L or if interferents are expected to exceed a total of 1000 mg/L in the digestate.

Note: For solid digestions, the volume reduction stage is critical to obtain accurate data. Close monitoring of each sample is necessary when this critical stage in the digestion is reached.

7.2 Prepare samples for hydride analysis by adding 1.00 g urea, and 20 mL concentrated HCl to a 5.00 mL aliquot of digested sample in a 50-mL volumetric flask. Heat in a water bath to dissolve salts and reduce selenium (at least 30 minutes is suggested). Bring flask to volume with reagent water before analyzing. A ten-fold dilution correction must be made in the final concentration calculations.

7.3 Prepare working standards from the standard stock selenium solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25 µg Se/L.

7.4 If EP extracts (Method 1310) are being analyzed for selenium, the method of standard additions must be used. Spike appropriate amounts of working standard selenium solution to three 25 mL aliquots of each unknown. Spiking volumes should be kept less than 0.250 mL to avoid excessive spiking dilution errors.

7.5 Set up instrumentation and hydride generation apparatus and fill reagent containers. The sample and blank flows should be set around 4.2 mL/min, and the borohydride flow around 2.1 mL/min. The argon carrier gas flow is adjusted to about 200 mL/min. For the AA, use the 196.0-nm wavelength and 2.0-nm slit width (or manufacturer's recommended slit-width) with background correction. Begin all flows and allow the instrument to warm-up according to the instrument manufacturer's instructions.

7.6 Place sample feed line into a prepared sample solution and start pump to begin hydride generation. Wait for a maximum steady-state signal on the strip-chart recorder. Switch to blank sample and watch for signal to decline to baseline before switching to the next sample and beginning the next analysis. Run standards first (low to high), then unknowns. Include appropriate QA/QC solutions, as required. Prepare calibration curves and convert absorbances to concentration. See following analytical flowchart.

CAUTION: The hydride of selenium is very toxic. Precautions must be taken to avoid inhaling the gas.

7.7 If the method of standard additions was employed, plot the measured concentration of the spiked samples and unspiked sample versus the spiked concentrations. The spiked concentration axis intercept will be the method of standard additions concentration. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration is determined from a standard calibration curve.

8.0 QUALITY CONTROL

8.1 Refer to Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

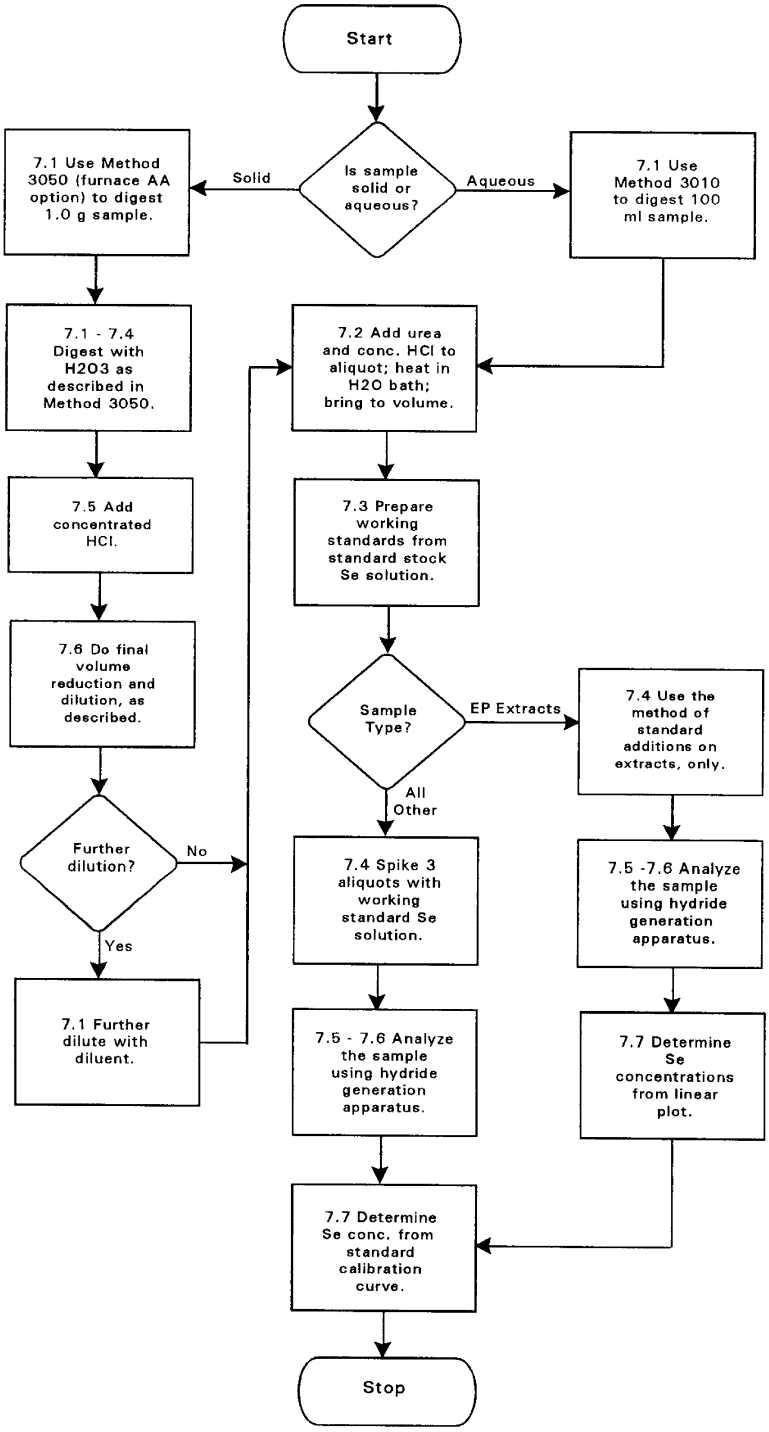
9.1 The relative standard deviation obtained by a single laboratory for 7 replicates of a contaminated soil was 18% for selenium at 8.2 ug/L in solution. The average percent recovery of the analysis of an 2 µg/L spike on ten different samples is 100.5% for selenium.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.

2. "Evaluation of Hydride Atomic Absorption Methods for Antimony, Arsenic, Selenium, and Tin", an EMSL-LV internal report under Contract 68-03-3249, Job Order 70.16, prepared for T. A. Hinners by D. E. Dobb, and J. D. Lindner of Lockheed Engineering and Sciences Co., and L. V. Beach of the Varian Corporation.

METHOD 7742
SELENIUM (ATOMIC ABSORPTION, BOROHYDRIDE REDUCTION)



METHOD 7741A

SELENIUM (ATOMIC ABSORPTION, GASEOUS HYDRIDE)

1.0 SCOPE AND APPLICATION

1.1 Method 7741 is an atomic absorption procedure that is approved for determining the concentration of selenium in wastes, mobility-procedure extracts, soils, and ground water, provided that the sample matrix does not contain high concentrations of chromium, copper, mercury, silver, cobalt, or molybdenum. All samples must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine applicability of the method to a given waste. If interferences are present the analyst should consider using Method 7740.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric/sulfuric acid digestion procedure described in this method. Next, the selenium in the digestate is reduced to Se(IV) with tin chloride. The Se(IV) is then converted to a volatile hydride with hydrogen produced from a zinc/HCl or sodium borohydrate/HCl reaction.

2.2 The volatile hydride is swept into an argon-hydrogen flame located in the optical path of an atomic absorption spectrophotometer; the resulting absorbance is proportional to the selenium concentration.

2.3 The typical detection limit for this method is 0.002 mg/L.

3.0 INTERFERENCES

3.1 High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver can cause analytical interferences.

3.2 Traces of nitric acid left following the sample work-up can result in analytical interferences. Nitric acid must be distilled off the sample by heating the sample until fumes of SO_3 are observed.

3.3 Elemental selenium and many of its compounds are volatile; therefore, certain samples may be subject to losses of selenium during sample preparation.

4.0 APPARATUS AND MATERIALS

4.1 100-mL beaker.

4.2 Electric hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.3 A commercially available zinc slurry hydride generator or a generator constructed from the following material (see Figure 1):

4.3.1 Medicine dropper: Fitted into a size "0" rubber stopper capable of delivering 1.5 mL.

4.3.2 Reaction flask: 50-mL, pear-shaped, with two 14/20 necks (Scientific Glass, JM-5835).

4.3.3 Gas inlet-outlet tube: Constructed from a micro cold-finger condenser (JM-3325) by cutting the portion below the 14/20 ground-glass joint.

4.3.4 Magnetic stirrer: To homogenize the zinc slurry.

4.3.5 Polyethylene drying tube: 10-cm, filled with glass wool to prevent particulate matter from entering the burner.

4.3.6 Flow meter: Capable of measuring 1 liter/min.

4.4 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-800 nm, and provisions for interfacing with a strip-chart recorder and simultaneous background correction.

4.5 Burner: Recommended by the particular instrument manufacturer for the argon-hydrogen flame.

4.6 Selenium hollow cathode lamp or electrodeless discharge lamp.

4.7 Strip-chart recorder (optional).

5.0 REAGENTS

5.1 Reagent water: Water should be monitored for impurities. Reagent water will be interference free. All references to water will refer to reagent water.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.3 Concentrated sulfuric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.4 Concentrated hydrochloric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.5 Diluent: Add 100 mL 18 N H_2SO_4 and 400 mL concentrated HCl to 400 mL reagent water and dilute to a final volume of 1 liter with reagent water.

5.6 Potassium iodide solution: Dissolve 20 g KI in 100 mL reagent water.

5.7 Stannous chloride solution: Dissolve 100 g $SnCl_2$ in 100 mL of concentrated HCl.

5.8 Selenium standard stock solution: 1,000 mg/L solution may be purchased, or prepared as follows: Dissolve 0.3453 g of selenious acid (assay 94.6% of H_2SeO_3) in reagent water. Add to a 200-mL volumetric flask and bring to volume (1 mL = 1 mg Se).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation:

7.1.1 To a 50-mL aliquot of digested sample (or, in the case of extracts, a 50-mL sample) add 10 mL of concentrated HNO_3 and 12 mL of 18 N H_2SO_4. Evaporate the sample on a hot plate until white SO_3 fumes are observed (a volume of about 20 mL). Do not let it char. If it chars, stop the digestion, cool, and add additional HNO_3. Maintain an excess of HNO_3 (evidence of brown fumes) and do not let the solution darken because selenium may be reduced and lost. When the sample remains colorless or straw yellow during evolution of SO_3 fumes, the digestion is complete.

> Caution: Venting reaction vessels should be done with caution and only under a fume hood or well ventilated area.

7.1.2 Cool the sample, add about 25 mL reagent water, and again evaporate to SO_3 fumes just to expel oxides of nitrogen. Cool. Add 40 mL concentrated HCl and bring to a volume of 100 mL with reagent water.

7.2 Prepare working standards from the standard stock solutions. The following procedures provide standards in the optimum range.

7.2.1 To prepare a working stock solution, pipet 1 mL standard stock solution (see Paragraph 5.8) into a 1-liter volumetric flask. Bring to volume with reagent water containing 1.5 mL concentrated HNO_3/liter. The concentration of this solution is 1 mg Se/L (1 mL = 1 ug Se).

7.2.2 Prepare six working standards by transferring 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of the working stock solution (see Paragraph 7.2.1) into 100-mL volumetric flasks. Bring to volume with diluent. The concentrations of these working standards are 0, 5, 10, 15, 20, and 25 ug Se/L.

7.3 Standard additions:

7.3.1 Take the 15-, 20-, and 25-ug standards and transfer quantitatively 25 mL from each into separate 50-mL volumetric flasks. Add 10 mL of the prepared sample to each. Bring to volume with reagent water containing 1.5 mL HNO_3/liter.

7.3.2 Add 10 mL of prepared sample to a 50-mL volumetric flask. Bring to volume with reagent water containing 1.5 mL HNO_3/liter. This is the blank.

7.4 Follow the manufacturer's instructions for operating an argon-hydrogen flame. The argon-hydrogen flame is colorless; therefore, it may be useful to aspirate a low concentration of sodium to ensure that ignition has occurred.

7.5 The 196.0-nm wavelength shall be used for the analysis of selenium.

7.6 Transfer a 25-mL portion of the digested sample or standard to the reaction vessel. Add 0.5 mL $SnCl_2$ solution. Allow at least 10 min for the metal to be reduced to its lowest oxidation state. Attach the reaction vessel to the special gas inlet-outlet glassware. Fill the medicine dropper with 1.50 mL sodium borohydrate or zinc slurry that has been kept in suspension with the magnetic stirrer. Firmly insert the stopper containing the medicine dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce the zinc slurry or sodium borohydrate into the sample or standard solution. The metal hydride will produce a peak almost immediately. When the recorder pen returns partway to the base line, remove the reaction vessel.

8.0 QUALITY CONTROL

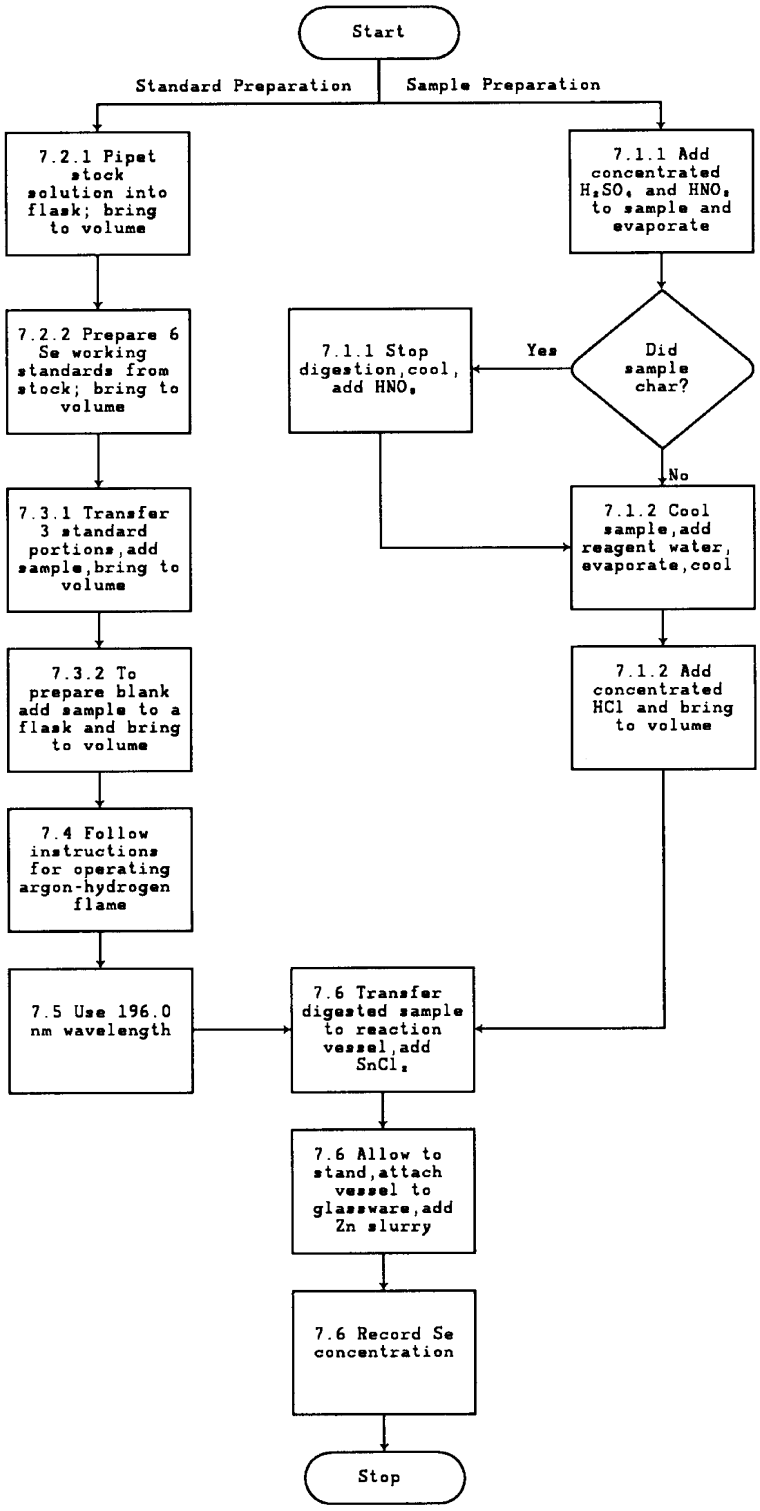
8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 270.3 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 270.3.


Start
Standard Preparation
Sample Preparation
7.2.1 Pipet stock solution into flask; bring to volume
7.2.2 Prepare 6 Se working standards from stock; bring to volume
7.3.1 Transfer 3 standard portions, add sample, bring to volume
7.3.2 To prepare blank add sample to a flask and bring to volume
7.4 Follow instructions for operating argon-hydrogen flame
7.5 Use 196.0 nm wavelength
7.1.1 Add concentrated H_2SO_4 and HNO_3 to sample and evaporate
Did sample char?
Yes
7.1.1 Stop digestion, cool, add HNO_3
No
7.1.2 Cool sample, add reagent water, evaporate, cool
7.1.2 Add concentrated HCl and bring to volume
7.6 Transfer digested sample to reaction vessel, add $SnCl_2$
7.6 Allow to stand, attach vessel to glassware, add Zn slurry
7.6 Record Se concentration
Stop

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical instrument detection limit (IDL) for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spiked samples.

3.3 Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 L/min air may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 L/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1 of reference 1 or according to the instrument manufacturers instructions. The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or
2. 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barneby and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

4.10 Hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.11 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent Water: Reagent water will be interference free. All references to water in this method refer to reagent water unless otherwise specified.

5.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1 liter.

5.4 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride can be substituted for stannous sulfate.

5.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.6 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

5.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg).

5.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Non-aqueous samples shall be refrigerated, when possible, and analyzed as soon as possible."

7.0 PROCEDURE

7.1 Sample preparation: Weigh triplicate 0.2-g portions of untreated sample and place in the bottom of a BOD bottle. Add 5 mL of reagent water and 5 mL of aqua regia. Heat 2 min in a water bath at 95°C. Cool; then add 50 mL reagent water and 15 mL potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

> CAUTION: Do this addition under a hood, as Cl_2 could be evolved. Add 55 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under step 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO^3 are added to the 0.2 g of sample. Add 5 mL of saturated $KMnO_4$ solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with reagent water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under step 7.4. Refer to the caution statement in section 7.1 for the proper protocol in reducing the excess permanganate solution and adding stannous sulfate.

7.3 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles or equivalent. Add enough reagent water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min in a water bath at 95°C. Allow the sample to cool; add 50 mL reagent water and 15 mL of $KMnO_4$ solution to each bottle and return to the water bath for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Step 7.4.

7.4 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration.

7.5 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve. Duplicates, spiked samples, and check standards should be routinely analyzed.

7.6 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.5 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

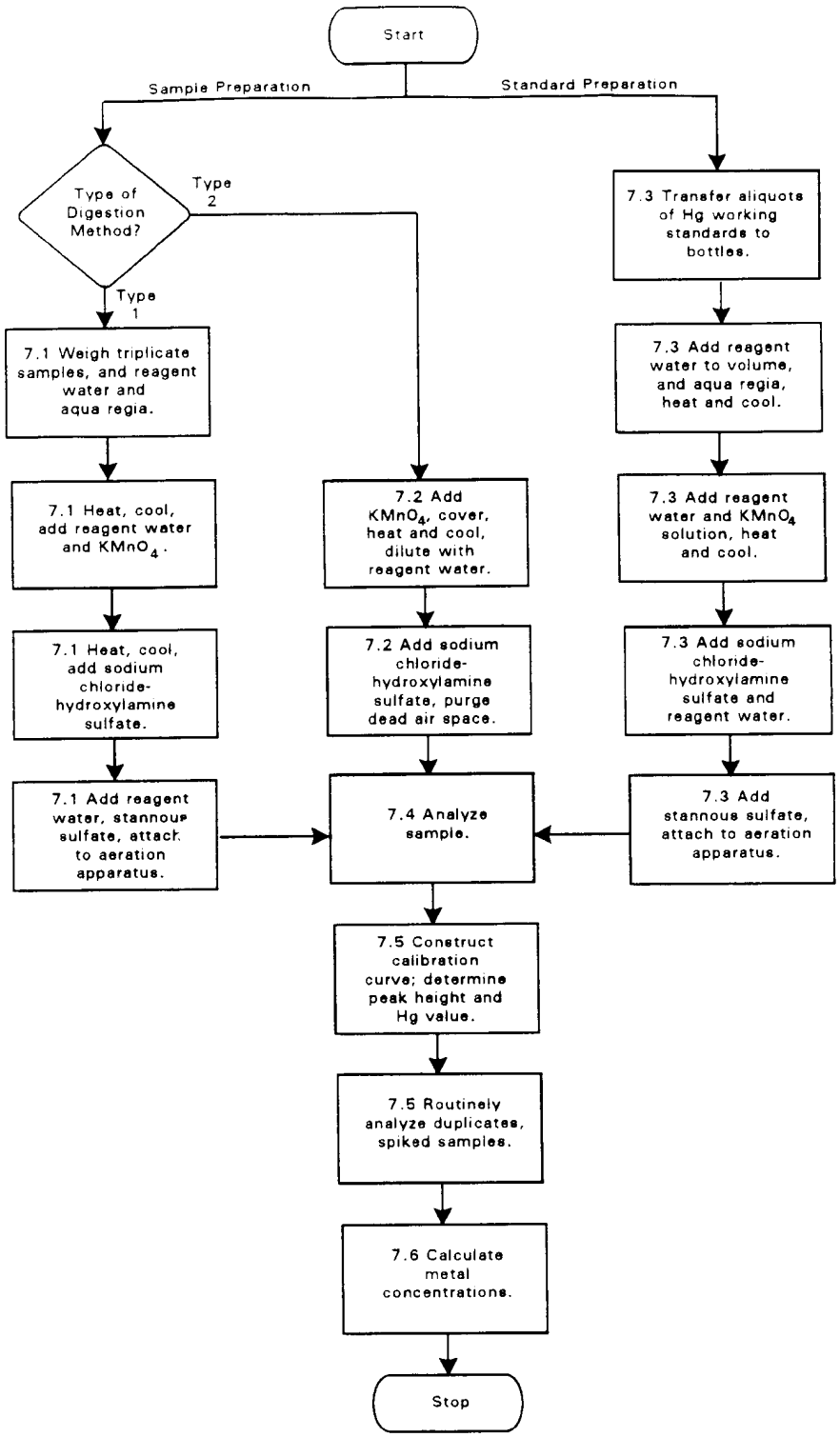
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.5.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	Not known	12, 12 ug/g
Wastewater treatment sludge	Not known	0.4, 0.28 ug/g


Start
Sample Preparation
Standard Preparation
Type of Digestion Method?
Type 2
Type 1
7.1 Weigh triplicate samples, and reagent water and aqua regia.
7.1 Heat, cool, add reagent water and $KMnO_4$.
7.1 Heat, cool, add sodium chloride-hydroxylamine sulfate.
7.1 Add reagent water, stannous sulfate, attach to aeration apparatus.
7.2 Add $KMnO_4$, cover, heat and cool, dilute with reagent water.
7.2 Add sodium chloride-hydroxylamine sulfate, purge dead air space.
7.3 Transfer aliquots of Hg working standards to bottles.
7.3 Add reagent water to volume, and aqua regia, heat and cool.
7.3 Add reagent water and $KMnO_4$ solution, heat and cool.
7.3 Add sodium chloride-hydroxylamine sulfate and reagent water.
7.3 Add stannous sulfate, attach to aeration apparatus.
7.4 Analyze sample.
7.5 Construct calibration curve; determine peak height and Hg value.
7.5 Routinely analyze duplicates, spiked samples.
7.6 Calculate metal concentrations.
Stop

MERCURY IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the liquid samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1 of reference 1 or according to the instrument manufacturers instructions. The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4; or

2. 0.25% Iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

4.10 Hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.11 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent Water: Reagent water will be interference free. All references to water in this method will refer to reagent water unless otherwise specified.

5.2 Sulfuric acid (H_2SO_4), concentrated: Reagent grade.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter.

5.4 Nitric acid (HNO_3), concentrated: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

5.5 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N H_2SO_4. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

5.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

5.7 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

5.8 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 mL of reagent water.

5.9 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated HNO_3 and adjust the volume to 100.0 mL (1 mL = 1 mg Hg). Stock solutions may also be purchased.

5.10 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at

0.15% nitric acid. This acid should be added to the flask, as needed, before addition of the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with HNO_3. The suggested maximum holding times for mercury is 28 days.

6.4 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Transfer 100 mL, or an aliquot diluted to 100 mL, containing <1.0 g of mercury, to a 300-mL BOD bottle or equivalent. Add 5 mL of H_2SO_4 and 2.5 mL of concentrated HNO_3, mixing after each addition. Add 15 mL of potassium permanganate solution to each sample bottle. Sewage samples may require additional permanganate. Ensure that equal amounts of permanganate are added to standards and blanks. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 sec, add 5 mL of stannous sulfate, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.2 Standard preparation: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles. Add enough reagent water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 to each bottle. Add 15 mL of $KMnO_4$ solution to each bottle and allow to stand at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 sec, add 5 mL of the stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.3 Analysis: At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass

valve, remove the stopper and frit from the BOD bottle, and continue the aeration. Because of instrument variation refer to the manufacturers recommended operating conditions when using this method.

7.4 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve. Duplicates, spiked samples, and check standards should be routinely analyzed.

7.5 Calculate metal concentrations (1) by the method of standard additions, or (2) from a calibration curve. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

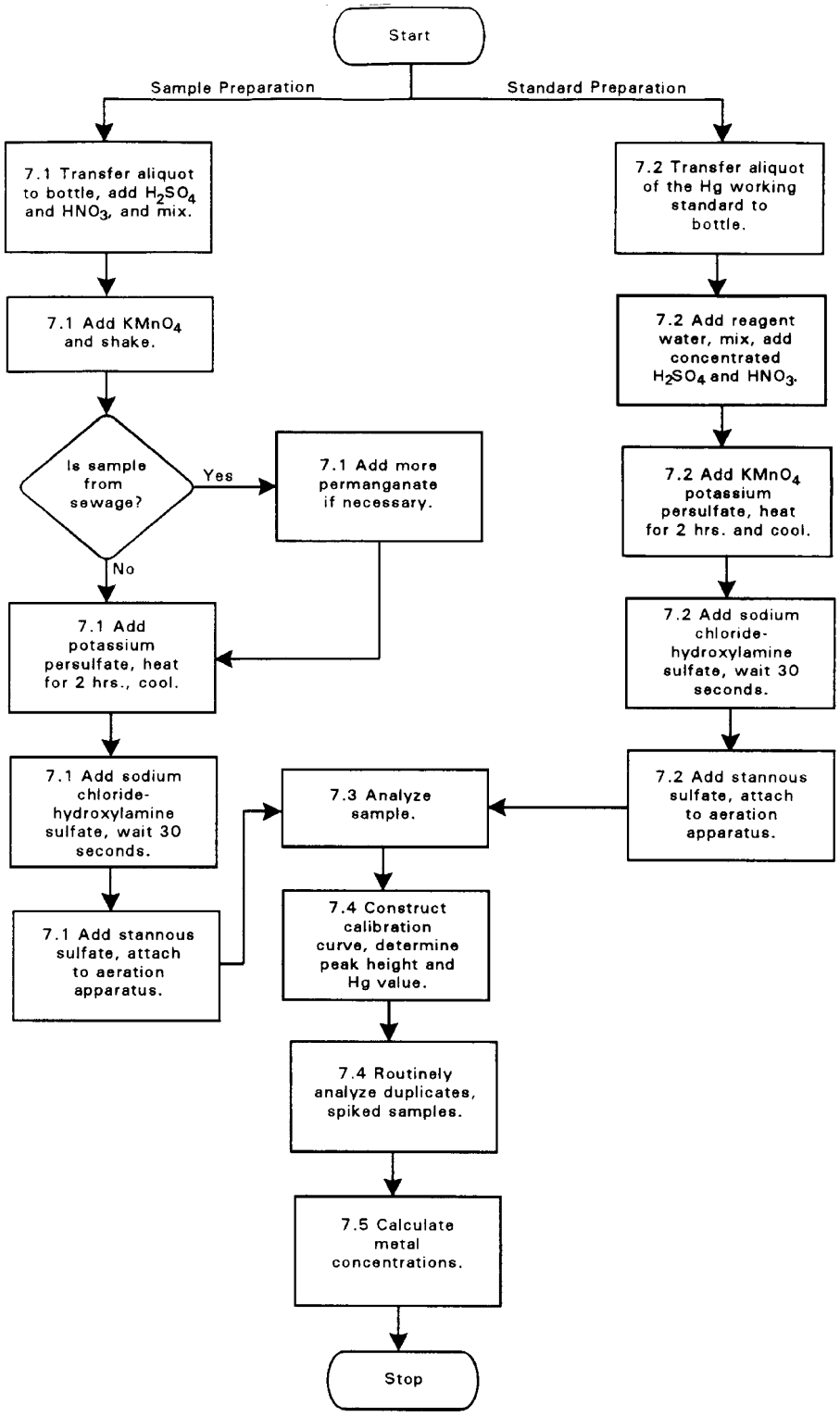
8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.1.


Start
Sample Preparation
Standard Preparation
7.1 Transfer aliquot to bottle, add H_2SO_4 and HNO_3, and mix.
7.1 Add $KMnO_4$ and shake.
Is sample from sewage?
Yes
No
7.1 Add more permanganate if necessary.
7.1 Add potassium persulfate, heat for 2 hrs., cool.
7.1 Add sodium chloride-hydroxylamine sulfate, wait 30 seconds.
7.1 Add stannous sulfate, attach to aeration apparatus.
7.2 Transfer aliquot of the Hg working standard to bottle.
7.2 Add reagent water, mix, add concentrated H_2SO_4 and HNO_3.
7.2 Add $KMnO_4$ potassium persulfate, heat for 2 hrs. and cool.
7.2 Add sodium chloride-hydroxylamine sulfate, wait 30 seconds.
7.2 Add stannous sulfate, attach to aeration apparatus.
7.3 Analyze sample.
7.4 Construct calibration curve, determine peak height and Hg value.
7.4 Routinely analyze duplicates, spiked samples.
7.5 Calculate metal concentrations.
Stop

METHOD 7197

CHROMIUM, HEXAVALENT (CHELATION/EXTRACTION)

1.0 SCOPE AND APPLICATION

1.1 Method 7197 is approved for determining the concentration of dissolved hexavalent chromium [Cr(VI)] in Extraction Procedure (EP) toxicity characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Paragraph 3.1).

1.2 Method 7197 may be used to analyze samples containing from 1.0 to 25 ug of Cr(VI) per liter.

2.0 SUMMARY OF METHOD

2.1 Method 7197 is based on the chelation of hexavalent chromium with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of an atomic absorption spectrophotometer.

3.0 INTERFERENCES

3.1 High concentrations of other metals may interfere.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Chromium hollow cathode lamp.

4.3 Strip-chart recorder (optional).

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Ammonium pyrrolidine dithiocarbamate (APDC) solution: Dissolve 1.0 g APDC in Type II water and dilute to 100 mL. Prepare fresh daily.

5.3 Bromphenol blue indicator solution: Dissolve 0.1 g bromphenol blue in 100 mL 50% ethanol.

5.4 Potassium dichromate standard solution I (1.0 mL = 100 ug Cr): Dissolve 0.2829 g pure dried potassium dichromate, $K_2Cr_2O_7$, in Type II water and dilute to 1,000 mL.

5.5 Potassium dichromate standard solution II (1.0 mL = 10.0 ug Cr): Dilute 100 mL chromium standard solution I to 1 liter with Type II water.

5.6 Potassium dichromate standard solution III (1.0 mL = 0.10 ug Cr): Dilute 10.0 mL chromium standard solution II to 1 liter with Type II water.

5.7 Methyl isobutyl ketone (MIBK), analytical reagent grade: Avoid or redistill material that comes in contact with metal or metal-lined caps.

5.8 Sodium hydroxide solution, 1 M: Dissolve to 40 g sodium hydroxide, NaOH (ASC reagent grade), in Type II water and dilute to 1 liter.

5.9 Sulfuric acid, 0.12 M: Slowly add 6.5 mL distilled reagent grade or spectrograde-quality sulfuric acid, H_2SO_4, to Type II water and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Because the stability of Cr(VI) in EP extracts is not completely understood at this time, the chelation and extraction should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, the samples and extracts should be stored at 4°C until analyzed.

7.0 PROCEDURE

7.1 Pipet a volume of extract containing less than 2.5 ug chromium (100 mL maximum) into a 200-mL volumetric flask and adjust the volume to approximately 100 mL.

7.2 Prepare a blank and sufficient standards and adjust the volume of each to approximately 100 mL.

7.3 Add 2 drops of bromphenol blue indicator solution. (The adjustment of pH to 2.4, Step 7.4, may be made with a pH meter instead of using an indicator.)

7.4 Adjust the pH by addition of 1 M NaOH solution dropwise until a blue color persists. Add 0.12 M H_2SO_4 dropwise until the blue color just disappears in both the standards and sample. Then add 2.0 mL of 0.12 M H_2SO_4 in excess. The pH at this point should be 2.4.

7.5 Add 5.0 mL APDC solution and mix. The pH should then be approximately 2.8.

7.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

7.7 Allow the layers to separate and add Type II water until the ketone layer is completely in the neck of the flask.

7.8 Aspirate the ketone layer and record the scale reading for each sample and standard against the blank. Repeat, and average the duplicate results.

7.9 Determine the mg/liter of Cr(VI) in each sample from a plot of scale readings of standards. A working curve must be prepared with each set of samples.

7.10 Verification:

7.10.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting chelation. This must be accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstances should the increase be less than 30 ug/L Cr(VI). To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.10.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

7.10.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

7.10.4 If the interference persists after sample dilution, an alternative method (Method 7195, Coprecipitation, or Method 7196, Colorimetric) should be used.

7.11 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

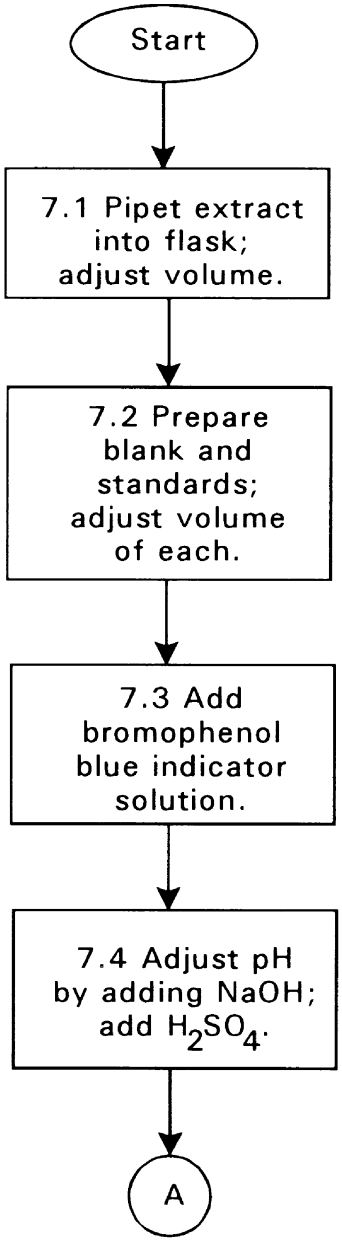
8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

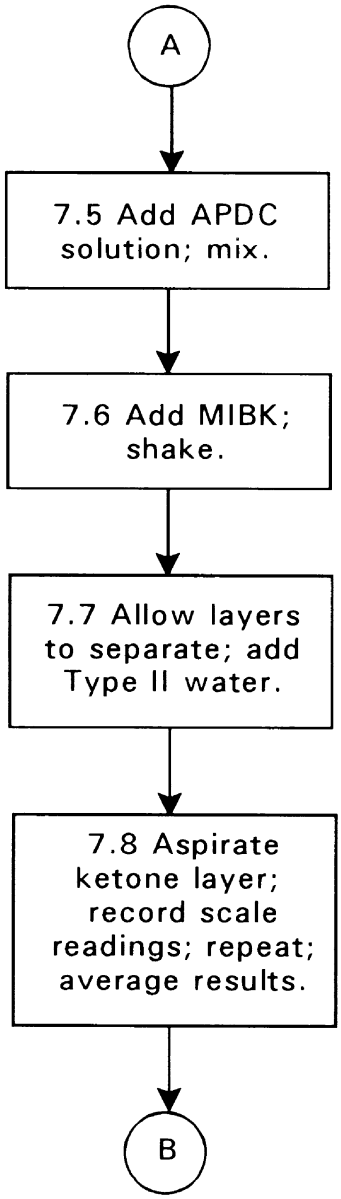
9.0 METHOD PERFORMANCE

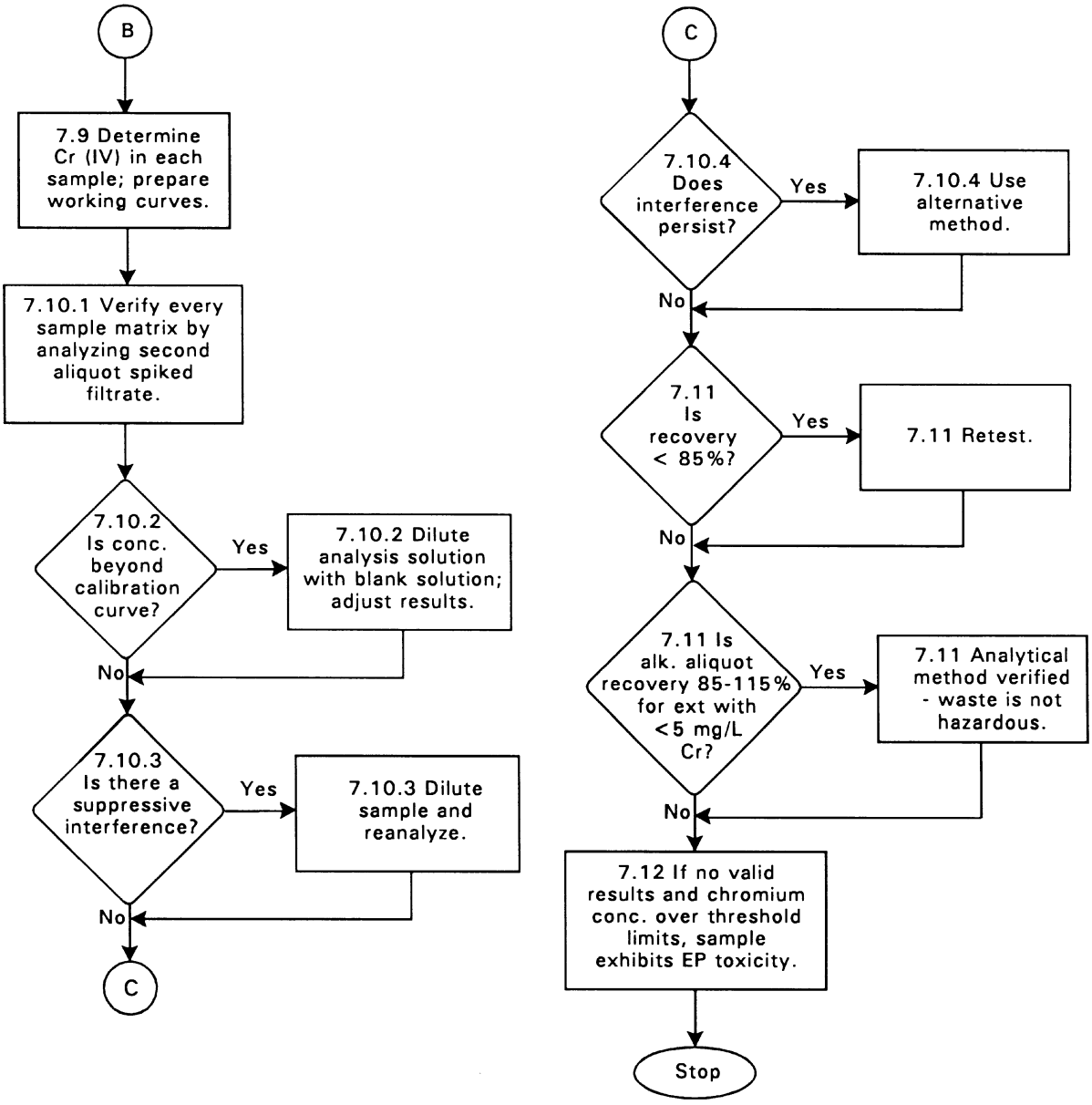
9.1 Precision and accuracy data are available in Method 218.4 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.4.


Start
7.1 Pipet extract into flask; adjust volume.
7.2 Prepare blank and standards; adjust volume of each.
7.3 Add bromophenol blue indicator solution.
7.4 Adjust pH by adding NaOH; add H_2SO_4.
A


A
7.5 Add APDC solution; mix.
7.6 Add MIBK; shake.
7.7 Allow layers to separate; add Type II water.
7.8 Aspirate ketone layer; record scale readings; repeat; average results.
B


B
7.9 Determine Cr (IV) in each sample; prepare working curves.
7.10.1 Verify every sample matrix by analyzing second aliquot spiked filtrate.
7.10.2 Is conc. beyond calibration curve?
Yes
7.10.2 Dilute analysis solution with blank solution; adjust results.
No
7.10.3 Is there a suppressive interference?
Yes
7.10.3 Dilute sample and reanalyze.
No
C
C
7.10.4 Does interference persist?
Yes
7.10.4 Use alternative method.
No
7.11 Is recovery < 85%?
Yes
7.11 Retest.
No
7.11 Is alk. aliquot recovery 85-115% for ext with <5 mg/L Cr?
Yes
7.11 Analytical method verified - waste is not hazardous.
No
7.12 If no valid results and chromium conc. over threshold limits, sample exhibits EP toxicity.
Stop

METHOD 7196A

CHROMIUM, HEXAVALENT (COLORIMETRIC)

1.0 SCOPE AND APPLICATION

1.1 Method 7196 is used to determine the concentration of dissolved hexavalent chromium [Cr(VI)] in EP/TCLP characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Paragraph 3.1 below).

1.2 Method 7196 may be used to analyze samples containing from 0.5 to 50 mg of Cr(VI) per liter.

2.0 SUMMARY OF METHOD

2.1 Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet color of unknown composition is produced. The reaction is very sensitive, the absorbancy index per gram atom of chromium being about 40,000 at 540 nm. Addition of an excess of diphenylcarbazide yields the red-violet product, and its absorbance is measured photometrically at 540 nm.

3.0 INTERFERENCES

3.1 The chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/L of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble.

3.2 Iron in concentrations greater than 1 mg/L may produce a yellow color, but the ferric iron color is not strong and difficulty is not normally encountered if the absorbance is measured photometrically at the appropriate wavelength.

4.0 APPARATUS AND MATERIALS

4.1 Colorimetric equipment: One of the following is required: Either a spectrophotometer, for use at 540 nm, providing a light path of 1 cm or longer, or a filter photometer, providing a light path of 1 cm or longer and equipped with a greenish-yellow filter having maximum transmittance near 540 nm.

5.0 REAGENTS

5.1 Reagent water: Reagent water should be monitored for impurities.

5.2 Potassium dichromate stock solution: Dissolve 141.4 mg of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in reagent water and dilute to 1 liter (1 mL = 50 ug Cr).

5.3 Potassium dichromate standard solution: Dilute 10.00 mL potassium dichromate stock solution to 100 mL (1 mL = 5 ug Cr).

5.4 Sulfuric acid, 10% (v/v): Dilute 10 mL of distilled reagent grade or spectrograde quality sulfuric acid, H_2SO_4, to 100 mL with reagent water.

5.5 Diphenylcarbazide solution: Dissolve 250 mg 1,5-diphenylcarbazide in 50 mL acetone. Store in a brown bottle. Discard when the solution becomes discolored.

5.6 Acetone (analytical reagent grade): Avoid or redistill material that comes in containers with metal or metal-lined caps.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Since the stability of Cr(VI) in extracts is not completely understood at this time, the analysis should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, the samples and extracts should be stored at 4°C until analyzed. The maximum holding time prior to analysis of the samples or extracts is 24 hr. The 24 hr holding time begins after extraction.

7.0 PROCEDURE

7.1 Color development and measurement: Transfer 95 mL of the extract to be tested to a 100-mL volumetric flask. Add 2.0 mL diphenylcarbazide solution and mix. Add H_2SO_4 solution to give a pH of 2 $\pm$ 0.5, dilute to 100 mL with reagent water, and let stand 5 to 10 min for full color development. Transfer an appropriate portion of the solution to a 1-cm absorption cell and measure its absorbance at 540 nm. Use reagent water as a reference. Correct the absorbance reading of the sample by subtracting the absorbance of a blank carried through the method (see Note below). An aliquot of the sample containing all reagents except diphenylcarbazide should be prepared and used to correct the sample for turbidity (i.e., a turbidity blank). From the corrected absorbance, determine the mg/L of chromium present by reference to the calibration curve.

NOTE: If the solution is turbid after dilution to 100 mL in Step 7.1, above, take an absorbance reading before adding the carbazide

reagent and correct the absorbance reading of the final colored solution by subtracting the absorbance measured previously.

7.2 Preparation of calibration curve:

7.2.1 To compensate for possible slight losses of chromium during digestion or other operations of the analysis, treat the chromium standards by the same procedure as the sample. Accordingly, pipet a chromium standard solution in measured volumes into 250-mL beakers or conical flasks to generate standard concentrations ranging from 0.5 to 5 mg/L Cr(VI) when diluted to the appropriate volume.

7.2.2 Develop the color of the standards as for the samples. Transfer a suitable portion of each colored solution to a 1-cm absorption cell and measure the absorbance at 540 nm. As reference, use reagent water. Correct the absorbance readings of the standards by subtracting the absorbance of a reagent blank carried through the method. Construct a calibration curve by plotting corrected absorbance values against mg/L of Cr(VI).

7.3 Verification:

7.3.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting color development. This must be accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstances should the increase be less than 30 µg Cr(VI)/liter. To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.3.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

7.3.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

7.3.4 If the interference persists after sample dilution, an alternative method (Method 7195, Coprecipitation, or Method 7197, Chelation/Extraction) should be used.

7.4 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified.

7.5 Analyze all extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions (see Method 7000, Section 8.7).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. Refer to Chapter One for more information.

8.2 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.3 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.4 Verify calibration with an independently prepared check standard every 15 samples.

8.5 Run one matrix spike replicate or one replicate sample for every ten samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process. Refer to Chapter One for more information concerning matrix spikes and matrix spike duplicates.

8.6 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

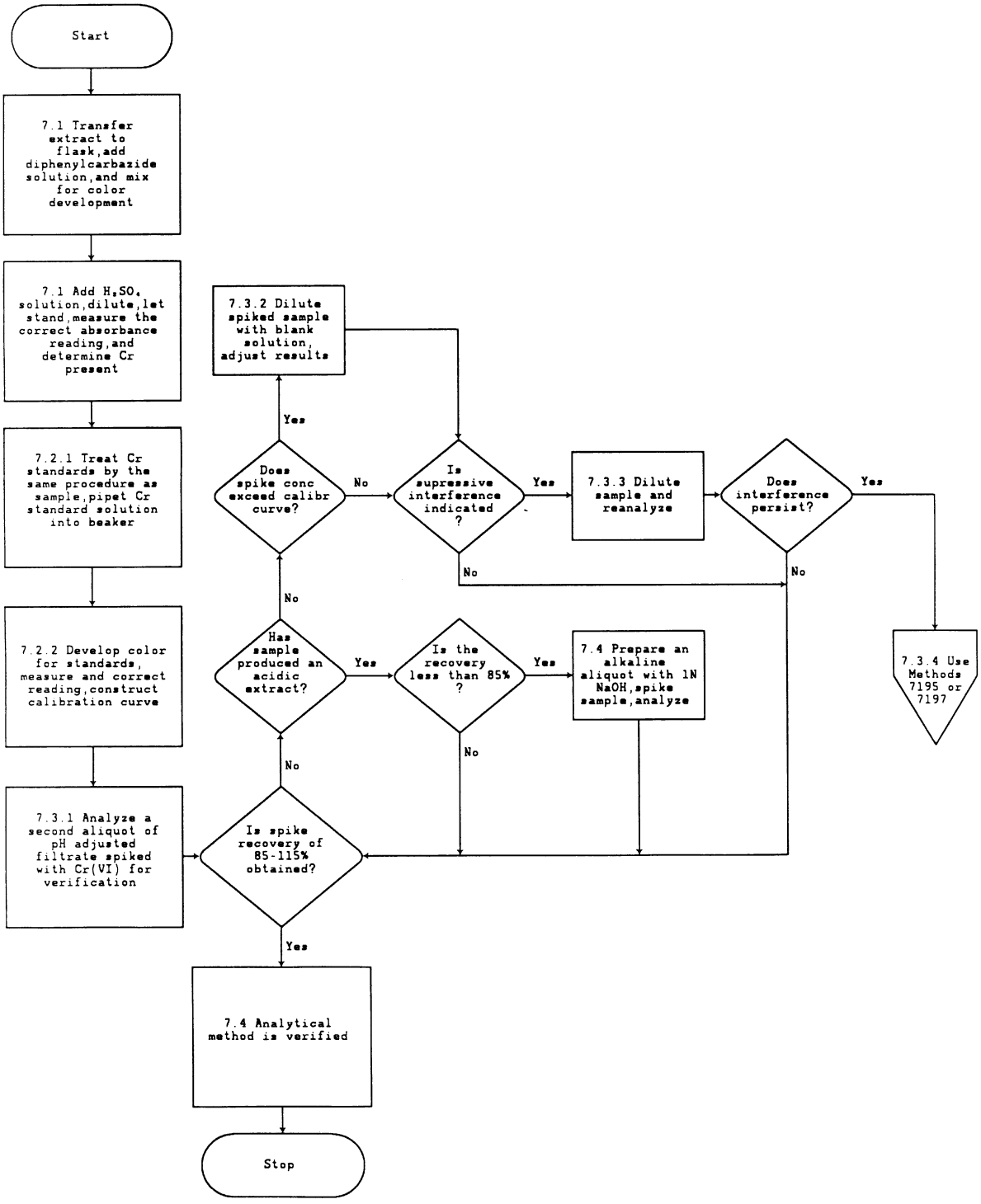
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Methods 218.4 and 218.5.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	Not known	0.096, 0.107 ug/g
Sediment from chemical storage area	3060	115, 117 ug/g


Start
7.1 Transfer extract to flask, add diphenylcarbazide solution, and mix for color development
7.1 Add H_2SO_4 solution, dilute, let stand, measure the correct absorbance reading, and determine Cr present
7.2.1 Treat Cr standards by the same procedure as sample, pipet Cr standard solution into beaker
7.2.2 Develop color for standards, measure and correct reading, construct calibration curve
7.3.1 Analyze a second aliquot of pH adjusted filtrate spiked with Cr(VI) for verification
7.3.2 Dilute spiked sample with blank solution, adjust results
Does spike conc exceed calibr curve?
Yes
No
Is supressive interference indicated ?
Yes
No
7.3.3 Dilute sample and reanalyze
Does interference persist?
Yes
No
7.3.4 Use Methods 7195 or 7197
Has sample produced an acidic extract?
Yes
No
Is the recovery less than 85% ?
Yes
No
7.4 Prepare an alkaline aliquot with 1N NaOH, spike sample, analyze
Is spike recovery of 85-115% obtained?
Yes
7.4 Analytical method is verified
Stop

Revision 1

METHOD 7195

CHROMIUM, HEXAVALENT (COPRECIPITATION)

1.0 SCOPE AND APPLICATION

1.1 Method 7195 is to be used to determine the concentration of dissolved hexavalent chromium [Cr(VI)] in Extraction Procedure (EP) toxicity characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Paragraph 3.1 below).

1.2 Method 7195 may be used to analyze samples containing more than 5 ug of Cr(VI) per liter. Either flame or furnace atomic absorption spectroscopy (Methods 7190 and 7191) can be used with coprecipitation.

2.0 SUMMARY OF METHOD

2.1 Method 7195 is based on the separation of Cr(VI) from solution by coprecipitation of lead chromate with lead sulfate in a solution of acetic acid. After separation, the supernate [containing Cr(III)] is drawn off and the precipitate is washed to remove occluded Cr(III). The Cr(VI) is then reduced and resolubilized in nitric acid and quantified as Cr(III) by either flame or furnace atomic absorption spectroscopy (Methods 7190 and 7191).

3.0 INTERFERENCES

3.1 Extracts containing either sulfate or chloride in concentrations above 1,000 mg/L should be diluted prior to analysis.

4.0 APPARATUS AND MATERIALS

4.1 Filtering flask: Heavy wall, 1-liter capacity.

4.2 Centrifuge tubes: Heavy duty, conical, graduated, glass-stoppered, 10-mL capacity.

4.3 Pasteur pipets: Borosilicate glass, 6.8 cm.

4.4 Centrifuge: Any centrifuge capable of reaching 2,000 rpm and accepting the centrifuge tubes described in Section 4.2 may be used.

4.5 pH meter: A wide variety of instruments are commercially available and suitable for this work.

4.6 Test tube mixer: Any mixer capable of imparting a thorough vortex is acceptable.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Lead nitrate solution: Dissolve 33.1 g of lead nitrate, $Pb(NO_3)2$ (analytical reagent grade), in Type II water and dilute to 100 mL.

5.3 Ammonium sulfate solution: Dissolve 2.7 g of ammonium sulfate, $(NH_4)_2SO_4$ (analytical reagent grade), in Type II water and dilute to 100 mL.

5.4 Calcium nitrate solution: Dissolve 11.8 g of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade), in Type II water and dilute to 100 mL (1 mL = 20 mg Ca).

5.5 Nitric acid: Concentrated, distilled reagent grade or spectrograde quality.

5.6 Acetic acid, glacial, 10% (v/v): Dilute 10 mL glacial acetic acid, CH_3COOH (ACS reagent grade), to 100 mL with Type II water.

5.7 Ammonium hydroxide, 10% (v/v): Dilute 10 mL concentrated ammonium hydroxide, NH_4OH (analytical reagent grade), to 100 mL with Type II water.

5.8 Hydrogen peroxide, 30%: ACS reagent grade.

5.9 Potassium dichromate standard solution: Dissolve 28.285 g of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in Type II water and dilute to 1 liter (1 mL = 10 mg Cr).

5.10 Trivalent chromium working stock solution: To 50 mL of the potassium dichromate standard solution, add 1 mL of 30% H_2O_2 and 1 mL concentrated HNO_3 and dilute to 100 mL with Type II water (1 mL = 5.0 mg trivalent chromium). Prepare fresh monthly, or as needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Since the stability of Cr(VI) in EP extracts is not completely understood at this time, the analysis should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, samples and extracts should be stored at 4°C until analyzed. The maximum holding time prior to analysis is 24 hr.

7.0 PROCEDURE

7.1 Transfer a 50-mL portion of the sample to a 100-mL Griffin beaker and adjust to a pH of 3.5 ± 0.3 by adding volumes of 10% acetic acid dropwise. Proceed immediately to Step 7.2, taking no longer than 15 min between these steps.

NOTE: Care must be exercised not to take the pH below 3. If the pH is inadvertently lowered to <3, 10% NH_4OH should be used to readjust the pH to 3.5 ± 0.3.

7.2 Pipet a 10-mL aliquot of the adjusted sample into a centrifuge tube. Add 100 uL of the lead nitrate solution, stopper the tube, mix the sample, and allow to stand for 3 min.

7.3 After the formation of lead chromate, to help retain Cr(III) complex in solution, add 0.5 mL glacial acetic acid, stopper, and mix.

7.4 To provide adequate lead sulfate for coprecipitation, add 100 uL of ammonium sulfate solution, stopper, and mix.

7.5 Place the stoppered centrifuge tube in the centrifuge, making sure that the tube is properly counterbalanced. Start the centrifuge and slowly increase the speed to 2,000 rpm in small increments over a period of 5 min. Hold at 2,000 rpm for 1 min.

NOTE: The speed of the centrifuge must be increased slowly to ensure complete coprecipitation.

7.6 After centrifuging, remove the tube and withdraw and discard the supernate using either the apparatus detailed in Figure 1 or careful decantation. If using the vacuum apparatus, the pasteur pipet is lowered into the tube and the supernate is sucked over into the filtering flask. With care, the supernate can be withdrawn to within approximately 0.1 mL above the precipitate. Wash the precipitate with 5 mL Type II water and repeat steps 7.5 and 7.6; then proceed to 7.7.

7.7 To the remaining precipitate, add 0.5 mL concentrated HNO_3, 100 uL 30% H_2O_2, and 100 uL calcium nitrate solution. Stopper the tube and mix, using a vortex mixer to disrupt the precipitate and solubilize the lead chromate. Dilute to 10 mL, mix, and analyze in the same manner as the calibration standard.

7.8 Flame atomic absorption: At the time of analysis, prepare a blank and a series of at least four calibration standards from the Cr(III) working stock that will adequately bracket the sample and cover a concentration range of 1 to 10 mg Cr/L. Add to the blank and each standard, before diluting to final volume, 1 mL 30% H_2O_2, 5 mL concentrated HNO_3, and 1 mL calcium nitrate solution for each 100 mL of prepared solution. These calibration standards should be prepared fresh weekly, or as needed. Refer to Method 7090 for more detail.

7.9 Furnace atomic absorption: At the time of analysis, prepare a blank and a series of at least four calibration standards from the Cr(III) working stock that will adequately bracket the sample and cover a concentration range of 5 to 100 ug Cr/L. Add to the blank and each standard, before diluting to final volume, 1 mL 30% H_2O_2, 5 mL concentrated HNO_3, and 1 mL calcium nitrate solution for each 100 mL of prepared solution. These calibration standards should be prepared fresh weekly, or as needed. Refer to Method 7191 for more detail.

7.10 Verification:

7.10.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting precipitation. This must be accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstance should the increase be less than 30 ug/L Cr(VI). To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.10.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

7.10.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed. If necessary, use furnace atomic absorption to achieve the optimal concentration range.

7.10.4 If the interference persists after sample dilution, an alternative method (Method 7197, Chelation/Extraction, or Method 7196, Colorimetric) should be used.

7.11 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

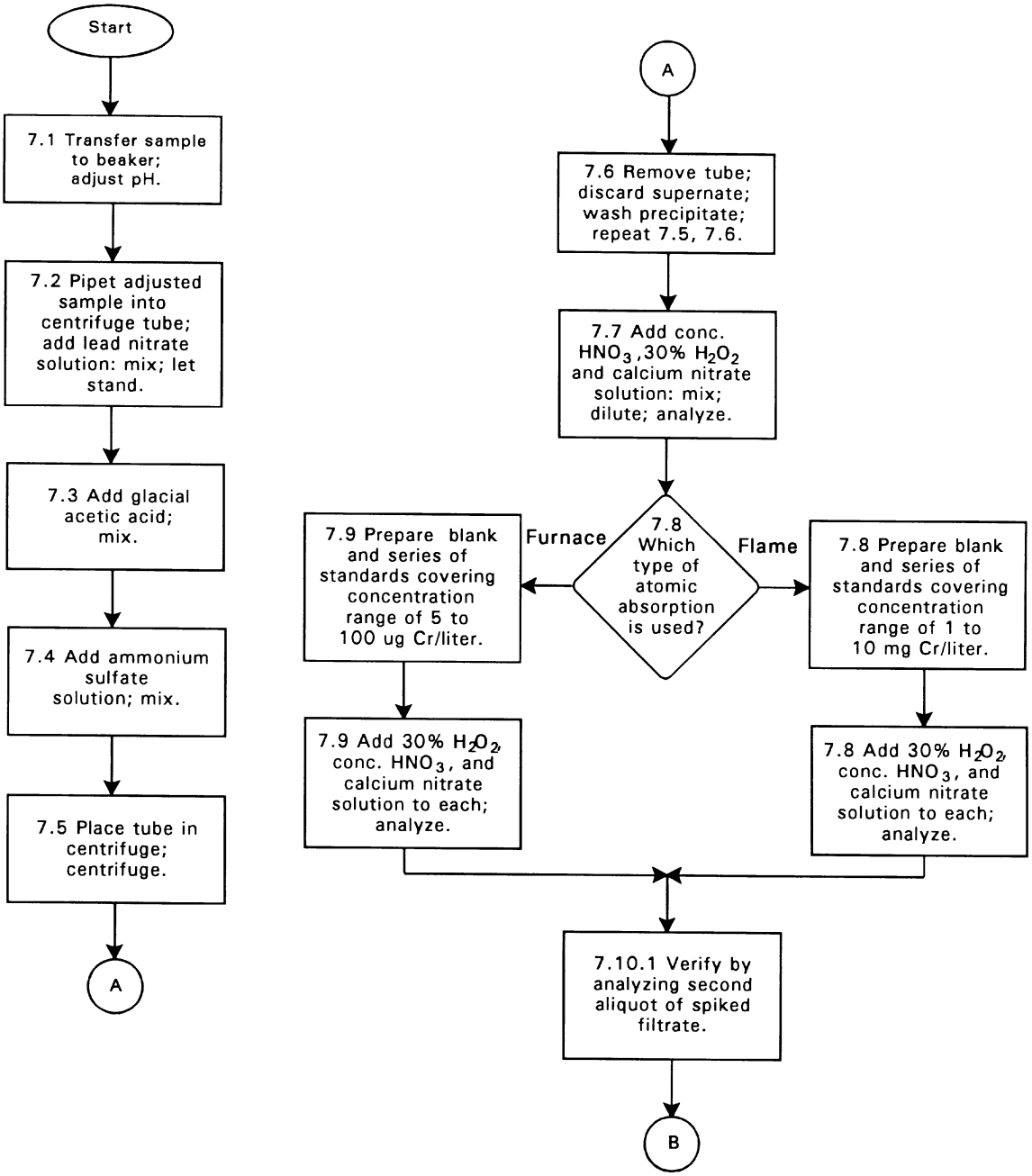
8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

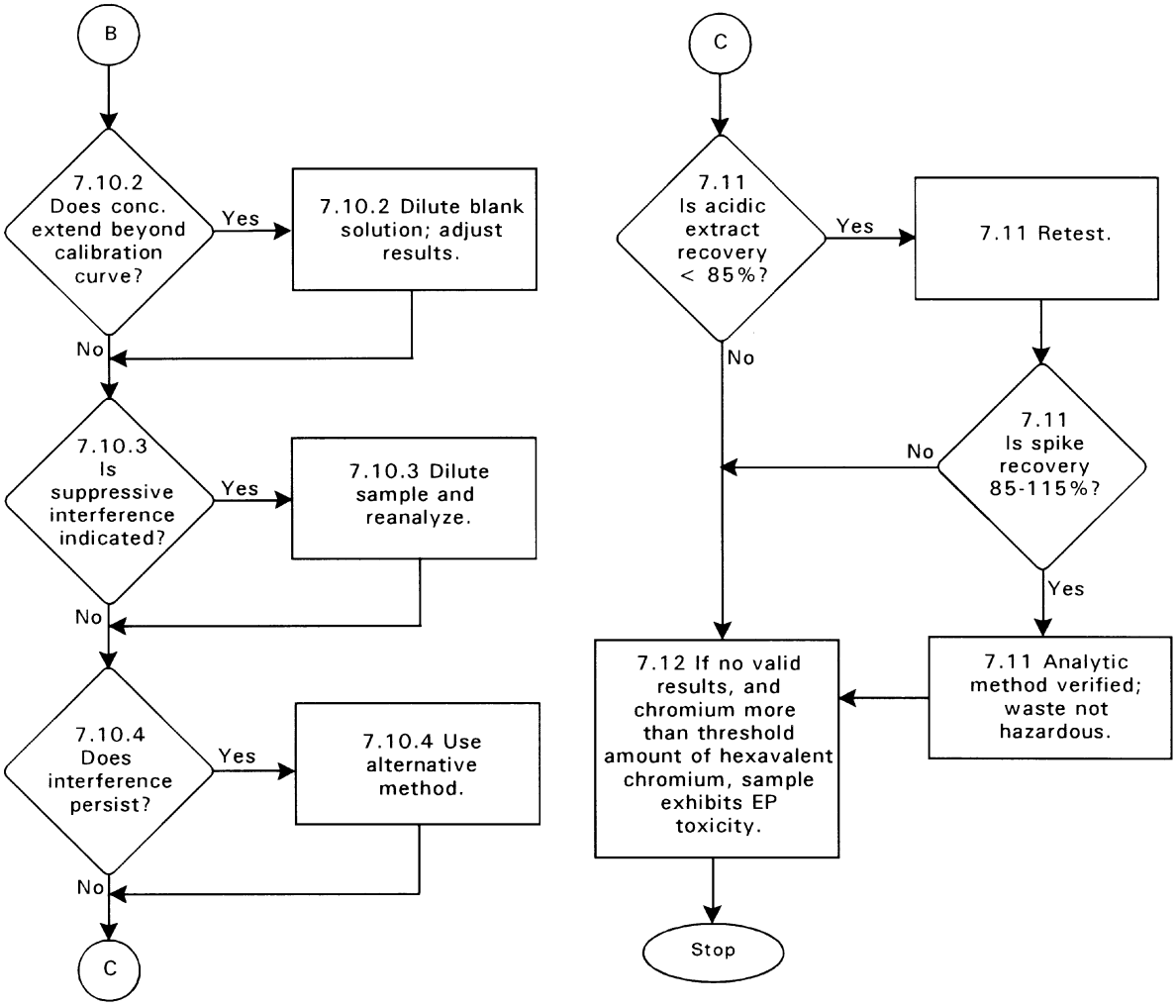
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 218.5 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.5.


Start
7.1 Transfer sample to beaker; adjust pH.
7.2 Pipet adjusted sample into centrifuge tube; add lead nitrate solution: mix; let stand.
7.3 Add glacial acetic acid; mix.
7.4 Add ammonium sulfate solution; mix.
7.5 Place tube in centrifuge; centrifuge.
A
A
7.6 Remove tube; discard supernate; wash precipitate; repeat 7.5, 7.6.
7.7 Add conc. HNO_3, 30% H_2O_2 and calcium nitrate solution: mix; dilute; analyze.
7.8 Which type of atomic absorption is used?
Furnace
Flame
7.9 Prepare blank and series of standards covering concentration range of 5 to 100 ug Cr/liter.
7.8 Prepare blank and series of standards covering concentration range of 1 to 10 mg Cr/liter.
7.9 Add 30% H_2O_2, conc. HNO_3, and calcium nitrate solution to each; analyze.
7.8 Add 30% H_2O_2, conc. HNO_3, and calcium nitrate solution to each; analyze.
7.10.1 Verify by analyzing second aliquot of spiked filtrate.
B


B
7.10.2 Does conc. extend beyond calibration curve?
Yes
7.10.2 Dilute blank solution; adjust results.
No
7.10.3 Is suppressive interference indicated?
Yes
7.10.3 Dilute sample and reanalyze.
No
7.10.4 Does interference persist?
Yes
7.10.4 Use alternative method.
No
C
C
7.11 Is acidic extract recovery < 85%?
Yes
7.11 Retest.
No
7.11 Is spike recovery 85-115%?
No
Yes
7.11 Analytic method verified; waste not hazardous.
7.12 If no valid results, and chromium more than threshold amount of hexavalent chromium, sample exhibits EP toxicity.
Stop

METHOD 7062

ANTIMONY AND ARSENIC (ATOMIC ABSORPTION, BOROHYDRIDE REDUCTION)

1.0 SCOPE AND APPLICATION

1.1 Method 7062 is an atomic absorption procedure for determining 1 µg/L to 400 µg/L concentrations of antimony and arsenic in wastes, mobility procedure extracts, soils, and ground water. Method 7062 is approved for sample matrices that contain up to a total of 4000 mg/L concentrations of cobalt, copper, iron, mercury, or nickel. A solid sample can contain up to 40% by weight of the interferents before exceeding 4000 mg/L in a digested sample. All samples including aqueous matrices must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are used to determine the applicability of the method to a given waste.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric acid digestion procedure described in Method 3010 for aqueous and extract samples and the nitric/peroxide/hydrochloric acid digestion procedure described in Method 3050 (furnace AA option) for sediments, soils, and sludges. Excess peroxide is removed by evaporating samples to near dryness at the end of the digestion followed by degassing the samples upon addition of urea. L-cysteine is then added as a masking agent. Next, the antimony and arsenic in the digest are reduced to the trivalent forms with potassium iodide. The trivalent antimony and arsenic are then converted to volatile hydrides using hydrogen produced from the reaction of the acidified sample with sodium borohydride in a continuous-flow hydride generator.

2.2 The volatile hydrides are swept into, and decompose in, a heated quartz cell located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the arsenic or antimony concentration.

2.3 The typical detection limit for this method is 1.0 µg/L.

3.0 INTERFERENCES

3.1 Very high (>4000 mg/L) concentrations of cobalt, copper, iron, mercury, and nickel can cause analytical interferences through precipitation as reduced metals and associated blockage of transfer lines and fittings.

3.2 Traces of peroxides left following the sample work-up can result in analytical interferences. Peroxides must be removed by evaporating each sample to near dryness followed by reaction with urea and allowing sufficient time for degassing before analysis (see Sections 7.1 and 7.2).

3.3 Even after acid digestion, organic compounds will remain in the sample. These flame gases and these organic compounds can absorb at the analytical wavelengths and background correction must be used.

4.0 APPARATUS AND MATERIALS

4.1 Electric hot plate: Large enough to hold at least several 100 mL Pyrex digestion beakers.

4.2 A continuous-flow hydride generator: A commercially available continuous-flow sodium borohydride/HCl hydride generator or a generator constructed similarly to that shown in Figure 1 (P. S. Analytical or equivalent).

4.2.1 Peristaltic Pump: A four-channel, variable-speed peristaltic pump to permit regulation of liquid-stream flow rates (Ismatec Reglo-100 or equivalent). Pump speed and tubing diameters should be adjusted to provide the following flow rates: sample/blank flow = 4.2 mL/min; borohydride flow = 2.1 mL/min; and potassium iodide flow = 0.5 mL/min.

4.2.2 Sampling Valve (optional): A sampling valve (found in the P. S. Analytical Hydride Generation System or equivalent) that allows switching between samples and blanks (rinse solution) without introduction of air into the system will provide more signal stability.

4.2.3 Transfer Tubing and Connectors: Transfer tubing (1 mm I.D.), mixing T's, and connectors are made of a fluorocarbon (PFA or TFM) and are of compatible sizes to form tight, leak-proof connections (Latchat, Technicon, etc. flow injection apparatus accessories or equivalent).

4.2.4 Mixing Coil: A 20-turn coil made by wrapping transfer tubing around a 1-cm diameter by 5-cm long plastic or glass rod (see Figure 1).

4.2.5 Mixing Coil Heater, if appropriate: A 250-mL Erlenmeyer flask containing 100 mL of water heated to boiling on a dedicated one-beaker hotplate (Corning PC-35 or equivalent). The mixing coil in 4.2.4 is immersed in the boiling water to speed kinetics of the hydride forming reactions and increase solubility of interfering reduced metal precipitates.

4.2.6 Gas-Liquid Separator: A glass apparatus for collecting and separating liquid and gaseous products (P.T. Analytical accessory or equivalent) which allows the liquid fraction to drain to waste and gaseous products above the liquid to be swept by a regulated carrier gas (argon) out of the cell for analysis. To avoid undue carrier gas dilution, the gas volume above the liquid should not exceed 20 mL. See Figure 1 for an acceptable separator shape.

4.2.7 Condensor: Moisture picked up by the carrier gas must be removed before encountering the hot absorbance cell. The moist carrier

gas with the hydrides is dried by passing the gasses through a small (< 25 mL) volume condensor coil (Ace Glass Model 6020-02 or equivalent) that is cooled to 5°C by a water chiller (Neslab RTE-110 or equivalent). Cool tap-water in place of a chiller is acceptable.

4.2.8 Flow Meter/Regulator: A meter capable of regulating up to 1 L/min of argon carrier gas is recommended.

4.3 Absorbance Cell: A 17 cm or longer quartz tube T-cell (windowless is strongly suggested) is recommended, as shown in Figure 1 (Varian Model VGA-76 accessory or equivalent). The cell is held in place by a holder that positions the cell about 1 cm over a conventional AA air-acetylene burner head. In operation, the cell is heated to around 900°C.

4.4 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with an appropriate recording device.

4.5 Burner: As recommended by the particular instrument manufacturer for an air-acetylene flame. An appropriate mounting bracket attached to the burner that suspends the quartz absorbance cell between 1 and 2 cm above the burner slot is required.

4.6 Antimony and arsenic hollow cathode lamps or antimony and arsenic electrodeless discharge lamps and power supply. Super-charged hollow-cathode lamps or EDL lamps are recommended for maximum sensitivity.

4.7 Strip-chart recorder (optional): Connect to output of spectrophotometer.

5.0 REAGENTS

5.1 Reagent water: Water must be monitored for impurities. Refer to Chapter 1 for definition of Reagent water.

5.2 Concentrated nitric acid (HNO_3): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.3 30% Hydrogen peroxide (H_2O_2): Peroxide must be a tin-free grade.

5.4 Concentrated hydrochloric acid (HCl): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.5 Diluent solution: A 3% HCl solution in reagent water must be prepared as a diluent solution if excessive levels of analytes or interfering metals are found in the undiluted samples.

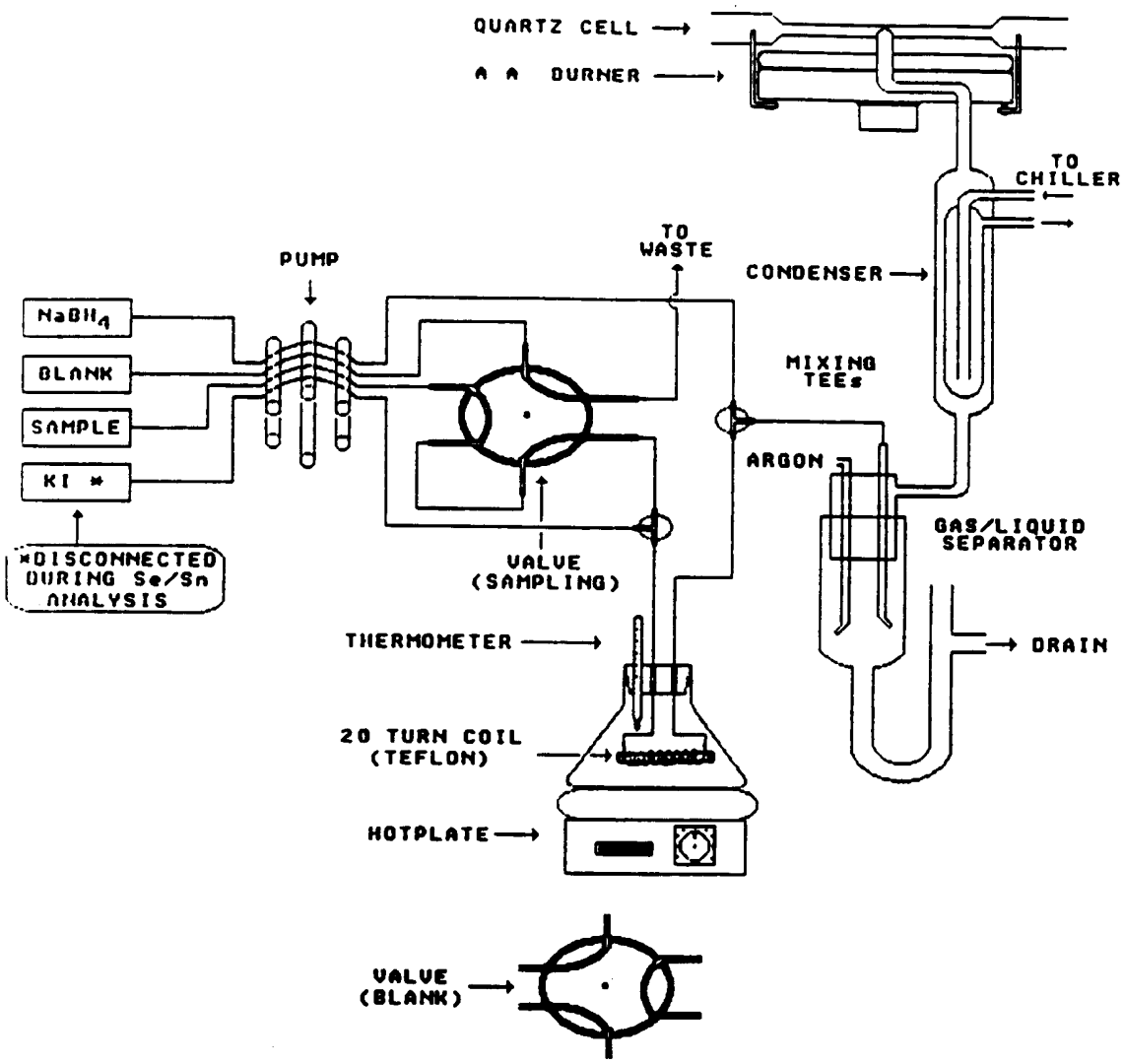


Figure 1. Continuous-flow sodium borohydride/hydride generator apparatus set-up and an AAS sample introduction system.

5.6 Urea (H_2NCONH_2): A 5.00-g portion of reagent grade urea must be added to a 25-mL aliquot of each sample for removal of excess peroxide through degassing (see Section 7.2).

5.7 L-cysteine ($C_6H_{12}N_2O_4S_2$): A 1.00-g portion of reagent grade L-cystine must be added to a 25-mL aliquot of each sample for masking the effects of suppressing transition metals (see Section 7.2).

5.8 20% Potassium iodide (KI): A 20% KI solution (20 g reagent-grade KI dissolved and brought to volume in 100 mL reagent water) must be prepared for reduction of antimony and arsenic to their +3 valence states.

5.9 4% Sodium borohydride ($NaBH_4$): A 4% sodium borohydride solution (20 g reagent-grade $NaBH_4$ plus 2 g sodium hydroxide dissolved in 500 mL of reagent water) must be prepared for conversion of the antimony and arsenic to their hydrides.

5.10 Analyte solutions:

5.10.1 **Antimony and arsenic stock standard solution** (1,000 mg/L): Either procure certified aqueous standards from a supplier and verify by comparison with a second standard, or dissolve 1.197 g of antimony trioxide Sb_2O_3 and 1.320 g of arsenic trioxide As_2O_3 in 100 mL of reagent water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter.

5.10.2 **Intermediate antimony and arsenic solution:** Pipet 1 mL stock antimony and arsenic solution into a 100-mL volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated HNO_3/liter (1 mL = 10 µg each of Sb and As).

5.10.3 **Standard antimony and arsenic solution:** Pipet 10 mL intermediate antimony and arsenic solution into a 100-mL volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated HNO_3/liter (1 mL = 1 µg each of Sb and As).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile antimony and arsenic compounds are suspected to be present in the samples.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Place a 100-mL portion of an aqueous sample or extract or 1.000 g of a dried solid sample in a 250-mL digestion beaker. Digest aqueous samples and extracts according to Method 3010. Digest solid samples according to Method 3050 (furnace AA option) with the following modifications: add 5 mL of concentrated hydrochloric acid just prior to the final volume reduction stage to aid in antimony recovery; the final volume reduction should be to less than 5 mL but not to dryness to adequately remove excess hydrogen peroxide (see note). After dilution to volume, further dilution with diluent may be necessary if analytes are known to exceed 400 µg/L or if interferents are expected to exceed 4000 mg/L in the digestate.

> Note: For solid digestions, the volume reduction stage is critical to obtain accurate data, especially for arsenic. Close monitoring of each sample is necessary when this critical stage is reached.

7.2 Prepare samples for hydride analysis by adding 5.00 g urea, 1.00 g L-cysteine, and 20 mL concentrated HCl to a 25-mL aliquot of digested sample in a 50-mL volumetric flask. Heat in a water bath until the L-cysteine has dissolved and effervescence has subsided (At least 30 minutes is suggested. If effervescense is still seen, repeat step 7.1 with more volume reduction.). Bring flask to volume with reagent water before analyzing. A 1:1 dilution correction must be made in the final concentration calculations.

7.3 Prepare working standards from the standard antimony and arsenic solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25 µg Sb and As/liter.

7.4 If EP extracts (Method 1310) are being analyzed for arsenic, the method of standard additions must be used. Spike appropriate amounts of intermediate or standard antimony and arsenic solution to three 25 mL aliquots of each unknown. Spiking volumes should be kept less than 0.250 mL to avoid excessive spiking dilution errors.

7.5 Set up instrumentation and hydride generation apparatus and fill reagent containers. The sample and blank flows should be set around 4.2 mL/min, the borohydride flow around 2.1 mL/min, and the potassium iodide flow around 0.5 mL/min. The argon carrier gas flow is adjusted to about 200 mL/min. For the AA, use the 217.6-nm wavelength and 0.7-nm slit width (or manufacturer's recommended slit-width) without background correction if analyzing for antimony. Use the 193.7-nm wavelength and 0.7-nm slit width (or manufacturer's recommended slit-width) with background correction for the analysis of arsenic. Begin all flows and allow 10 minutes for warm-up.

7.6 Place sample feed line into a prepared sample solution and start pump to begin hydride generation. Wait for a maximum steady-state signal on the strip-chart recorder or output meter. Switch to blank sample and watch for signal to decline to baseline before switching to the next sample and beginning the next analysis. Run standards first (low to high), then unknowns. Include appropriate QA/QC solutions, as required. Prepare calibration curves and convert absorbances to concentration. If a heating coil is not being used, KI must be added to the samples and heated for thirty minutes to ensure reduction.

CAUTION: The hydrides of antimony and arsenic are very toxic. Precautions must be taken to avoid inhaling the gas.

7.7 If the method of standard additions was employed, plot the measured concentration of the spiked samples and unspiked sample versus the spiked concentrations. The spiked concentration axis intercept will be the method of standard additions concentration. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration is determined from a standard calibration curve.

8.0 QUALITY CONTROL

8.1 See section 8.0 of Method 7000.

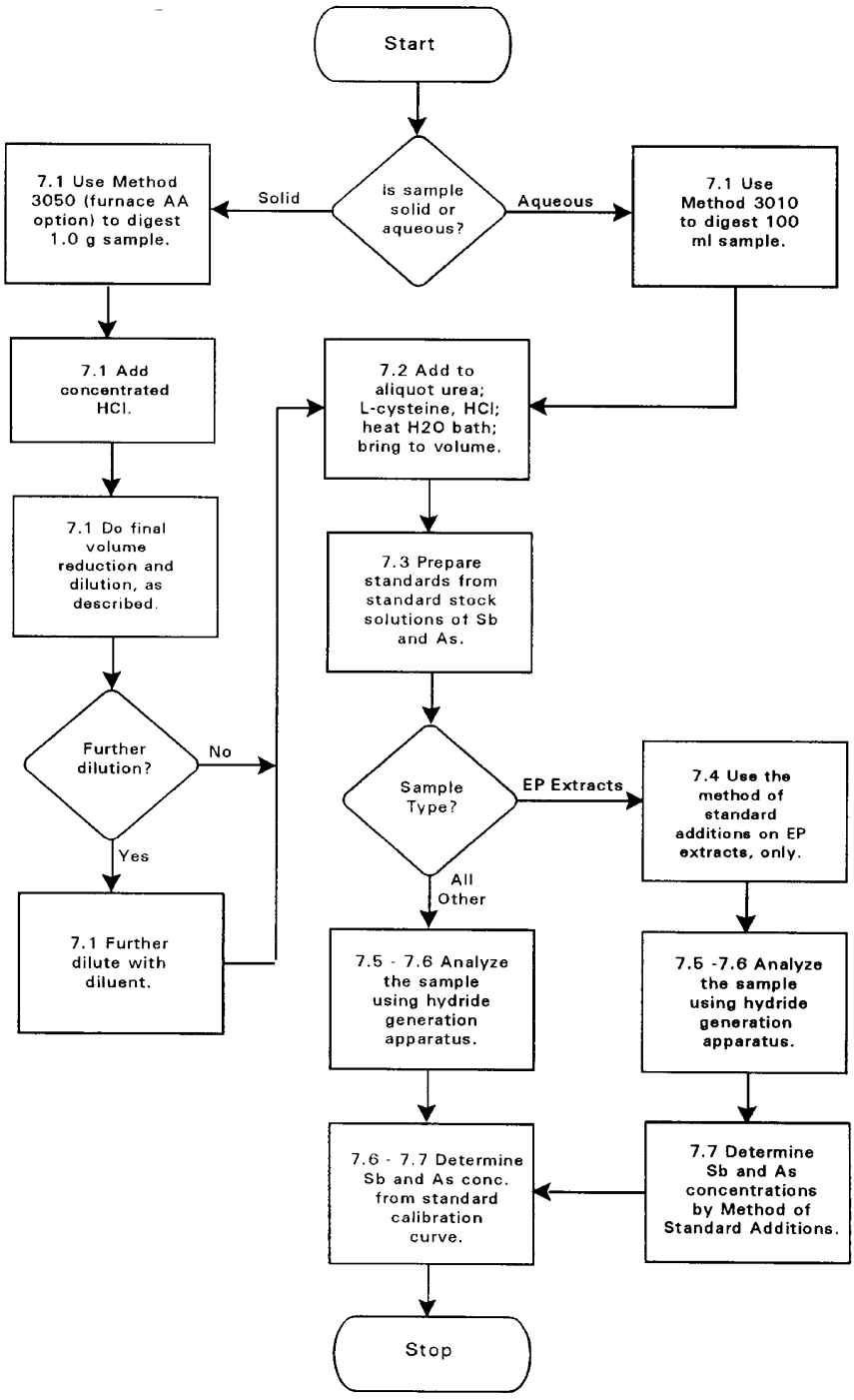
9.0 METHOD PERFORMANCE

9.1 The relative standard deviations obtained by a single laboratory for 7 replicates of a contaminated soil were 18% for antimony at 9.1 ug/L in solution and 4.6% for arsenic at 68 ug/L in solution. The average percent recovery of the analysis of an 8 µg/L spike on ten different samples is 103.7% for arsenic and 95.6% for antimony.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.

2. "Evaluation of Hydride Atomic Absorption Methods for Antimony, Arsenic, Selenium, and Tin", an EMSL-LV internal report under Contract 68-03-3249, Job Order 70.16, prepared for T. A. Hinners by D. E. Dobb, and J. D. Lindner of Lockheed Engineering and Sciences Co., and L. V. Beach of the Varian Corporation.


Start
is sample solid or aqueous?
Solid
Aqueous
7.1 Use Method 3050 (furnace AA option) to digest 1.0 g sample.
7.1 Use Method 3010 to digest 100 ml sample.
7.1 Add concentrated HCl.
7.2 Add to aliquot urea; L-cysteine, HCl; heat H2O bath; bring to volume.
7.1 Do final volume reduction and dilution, as described.
7.3 Prepare standards from standard stock solutions of Sb and As.
Further dilution?
No
Yes
Sample Type?
EP Extracts
All Other
7.4 Use the method of standard additions on EP extracts, only.
7.1 Further dilute with diluent.
7.5 - 7.6 Analyze the sample using hydride generation apparatus.
7.5 -7.6 Analyze the sample using hydride generation apparatus.
7.6 - 7.7 Determine Sb and As conc. from standard calibration curve.
7.7 Determine Sb and As concentrations by Method of Standard Additions.
Stop

METHOD 7061A

ARSENIC (ATOMIC ABSORPTION, GASEOUS HYDRIDE)

1.0 SCOPE AND APPLICATION

1.1 Method 7061 is an atomic absorption procedure for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and ground water. Method 7061A is approved only for sample matrices that do not contain high concentrations of chromium, copper, mercury, nickel, silver, cobalt, and molybdenum. All samples must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine the applicability of the method to a given waste.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric/sulfuric acid digestion procedure described in this method (Step 7.1). Next, the arsenic in the digestate is reduced to the trivalent form with tin chloride. The trivalent arsenic is then converted to a volatile hydride using hydrogen produced from a zinc/hydrochloric acid reaction.

2.2 The volatile hydride is swept into an argon-hydrogen flame located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the arsenic concentration.

2.3 The typical detection limit for this method is 0.002 mg/L.

3.0 INTERFERENCES

3.1 High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver can cause analytical interferences.

3.2 Traces of nitric acid left following the sample work-up can result in analytical interferences. Nitric acid must be distilled off by heating the sample until fumes of sulfur trioxide (SO_3) are observed.

3.3 Elemental arsenic and many of its compounds are volatile; therefore, certain samples may be subject to losses of arsenic during sample preparation.

4.0 APPARATUS AND MATERIALS

4.1 Beaker or equivalent - 100-mL.

4.2 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

4.3.1 Medicine dropper - Capable of fitting into a size "0" rubber stopper and delivering 1.5 mL.

4.3.2 Pear-shaped reaction flask - 50-mL, with two 14/20 necks (Scientific Glass JM-5835 or equivalent).

4.3.3 Gas inlet-outlet tube - Constructed from a micro cold-finger condenser (JM-3325) by cutting the portion below the 14/20 ground-glass joint.

4.3.4 Magnetic stirrer - To homogenize the zinc slurry.

4.3.5 Polyethylene drying tube - 10-cm, filled with glass to prevent particulate matter from entering the burner.

4.3.6 Flow meter - Capable of measuring 1 liter/min.

4.3.7 Class A volumetric flasks.

4.3.8 Graduated cylinder or equivalent.

4.4 Atomic absorption spectrophotometer - Single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip-chart recorder.

4.5 Burner - Recommended by the particular instrument manufacturer for the argon-hydrogen flame.

4.6 Arsenic hollow cathode lamp or arsenic electrodeless discharge lamp.

4.7 Strip-chart recorder.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water will be interferent free. All references to water in the method refer to reagent water unless otherwise specified.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine levels of impurities. If a method blank is < MDL, the acid can be used.

5.4 Sulfuric acid (concentrated), H_2SO_4. Acid should be analyzed to determine levels of impurities. If a method blank is < MDL, the acid can be used.

5.5 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine levels of impurities. If a method blank is < MDL, the acid can be used.

5.6 Diluent - Add 100 mL 18N H_2SO_4 and 400 mL concentrated HCl to 400 mL water and dilute to a final volume of 1 liter with water.

5.7 Potassium iodide solution - Dissolve 20 g KI in 100 mL water.

5.8 Stannous chloride solution - Dissolve 100 g $SnCl_2$ in 100 mL concentrated HCl.

5.9 Arsenic solutions

5.9.1 Arsenic standard solution (1,000 mg/L) - Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide As_2O_3 in 100 mL of water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter.

5.9.2 Intermediate arsenic solution - Pipet 1 mL stock arsenic solution into a 100-mL volumetric flask and bring to volume with water containing 1.5 mL concentrated HNO_3/liter (1 mL = 10 ug As).

5.9.3 Standard arsenic solution - Pipet 10 mL intermediate arsenic solution into a 100-mL volumetric flask and bring to volume with water containing 1.5 mL concentrated HNO_3/liter (1 mL = 1 ug As).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g. containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of < 2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Place a 50-mL aliquot of digested sample (or, in the case of analysis of EP extracts, 50 mL) of the material to be analyzed in a 100-mL beaker. Add 10 mL concentrated HNO_3 and 12 mL 18N H_2SO_4. Evaporate the sample in the hood on an electric hot plate until white SO_3 fumes are observed (a volume of about 20 mL). Do not let the sample char. If charring occurs, immediately turn off the heat, cool, and add an additional 3 mL of HNO_3. Continue to add additional HNO_3 in order to maintain an excess (as evidenced by the formation of brown fumes). Do not let the solution darken, because arsenic may be reduced and lost. When the sample remains colorless or straw yellow during evolution of SO_3 fumes, the digestion is complete. Cool the sample, add about 25 mL water, and again evaporate until SO_3 fumes are produced in order to expel oxides of nitrogen. Cool. Transfer the digested sample to a 100-mL volumetric flask. Add 40 mL of concentrated HCl and bring to volume with water.

7.2 Prepare working standards from the standard arsenic solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25 ug As/liter.

7.3 If EP extracts are being analyzed or if a matrix interference is encountered, take the 15-, 20-, and 25-mg/liter standards and quantitatively transfer 25 mL of each of these standards into separate 50-mL volumetric flasks. Add 10 mL of the prepared sample to each flask. Bring to volume with water containing 1.5 mL HCl/liter.

7.4 Add 10 mL of prepared sample to a 50-mL volumetric flask. Bring to volume with water containing 1.5 mL HCl/liter. This is the zero addition aliquot.

NOTE: The absorbance from the zero addition aliquot will be one-fifth that produced by the prepared sample. The absorbance from the spiked samples will be one-half that produced by the standards plus the contribution from one-fifth of the prepared sample. Keeping these absorbances in mind will assist in judging the correct dilutions to produce optimum absorbance.

7.5 Transfer a 25-mL portion of the digested sample or standard to the reaction vessel and add 1 mL KI solution. Add 0.5 mL $SnCl_2$ solution. Allow at least 10 minutes for the metal to be reduced to its lowest oxidation state. Attach the reaction vessel to the special gas inlet-outlet glassware. Fill the medicine dropper with 1.50 mL zinc slurry that has been kept in suspension with the magnetic stirrer. Firmly insert the stopper containing the medicine dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce the zinc slurry into the sample or standard solution. The metal hydride will produce a peak almost immediately. After the recorder pen begins to return to the base line, the reaction vessel can be removed.

CAUTION: Arsine is very toxic. Precautions must be taken to avoid inhaling arsine gas.

7.6 Use the 193.7-nm wavelength and background correction for the analysis of arsenic.

7.7 Follow the manufacturer's instructions for operating an argon-hydrogen flame. The argon-hydrogen flame is colorless; therefore, it may be useful to aspirate a low concentration of sodium to ensure that ignition has occurred.

7.8 If the method of standard additions was employed, plot the absorbances of spiked samples and blank vs. the concentrations. The extrapolated value will be one-fifth the concentration of the original sample. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration can be part of the calibration curve.

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 206.3 of Methods for Chemical Analysis of Water and Wastes.

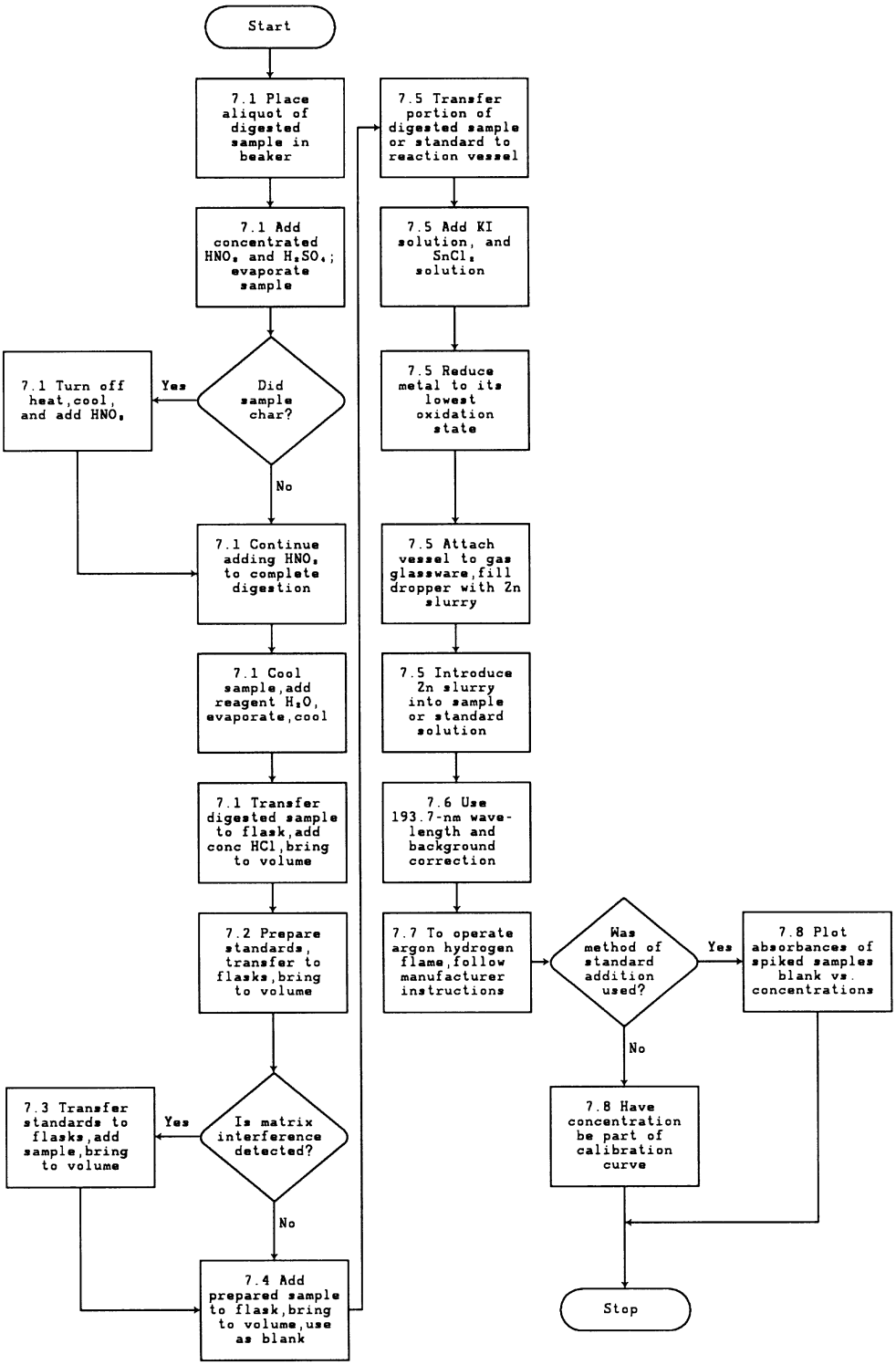
10.0 REFERENCES

1. Methods For Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.

2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

METHOD 7061A
ARSENIC (ATOMIC ABSORPTION, GASEOUS HYDRIDE)



METHOD 7000A

ATOMIC ABSORPTION METHODS

1.0 SCOPE AND APPLICATION

1.1 Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters and domestic and industrial wastes. While drinking water free of particulate matter may be analyzed directly, ground water, other aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion prior to analysis for both total and acid leachable metals. Analysis for dissolved elements does not require digestion if the sample has been filtered and acidified.

1.2 Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and models of atomic absorption spectrophotometers. The data shown in Table 1 provide some indication of the detection limits obtainable by direct aspiration and by furnace techniques. For clean aqueous samples, the detection limits shown in the table by direct aspiration may be extended downward with scale expansion and upward by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample and/or through solvent extraction techniques. For certain samples, lower concentrations may also be determined using the furnace techniques. The detection limits given in Table 1 are somewhat dependent on equipment (such as the type of spectrophotometer and furnace accessory, the energy source, the degree of electrical expansion of the output signal), and are greatly dependent on sample matrix. Detection limits should be established, empirically, for each matrix type analyzed. When using furnace techniques, however, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. To ensure valid data with furnace techniques, the analyst must examine each matrix for interference effects (see Step 3.2.1) and, if detected, treat them accordingly, using either successive dilution, matrix modification, or method of standard additions (see Step 8.7).

1.3 Where direct-aspiration atomic absorption techniques do not provide adequate sensitivity, reference is made to specialized procedures (in addition to the furnace procedure) such as the gaseous-hydride method for arsenic and selenium and the cold-vapor technique for mercury.

2.0 SUMMARY OF METHOD

2.1 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy, the technique generally is limited to metals in solution or solubilized through some form of sample processing.

2.2 Preliminary treatment of waste water, ground water, EP extracts, and industrial waste is always necessary because of the complexity and variability of sample matrix. Solids, slurries, and suspended material must be subjected to

a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Step 3.2 (Sample Preparation Methods).

2.3 In direct-aspiration atomic absorption spectroscopy, a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp or an electrodeless discharge lamp is directed through the flame into a monochromator, and onto a detector that measures the amount of absorbed light. Absorption depends upon the presence of free unexcited ground-state atoms in the flame. Because the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

2.4 When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms is vaporized and dissociated for absorption in the tube rather than the flame, the use of smaller sample volumes or detection of lower concentrations of elements is possible. The principle is essentially the same as with direct aspiration atomic absorption, except that a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground-state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground-state element in the vapor. The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace, thereby causing the injected specimen to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp or electrodeless discharge lamp, and a photosensitive device measures the attenuated transmitted radiation.

3.0 INTERFERENCES

3.1 Direct aspiration

3.1.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or when the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome phosphate interference in magnesium, calcium, and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

3.1.2 Chemical interferences may also be eliminated by separating the metal from the interfering material. Although complexing agents are employed primarily to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

3.1.3 The presence of high dissolved solids in the sample may result in an interference from nonatomic absorbance such as light scattering. If background correction is not available, a nonabsorbing wavelength should be checked. Preferably, samples containing high solids should be extracted.

3.1.4 Ionization interferences occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess (1,000 mg/L) of an easily ionized element such as K, Na, Li or Cs.

3.1.5 Spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Interference can also occur when resonant energy from another element in a multielement lamp, or from a metal impurity in the lamp cathode, falls within the bandpass of the slit setting when that other metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

3.1.6 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

3.1.7 All metals are not equally stable in the digestate, especially if it contains only nitric acid, not nitric acid and hydrochloric acid. The digestate should be analyzed as soon as possible, with preference given to Sn, Sb, Mo, Ba, and Ag.

3.2 Furnace procedure

3.2.1 Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical interferences. The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or chemical interference, the serial dilution technique (see Step 8.6) may be used. Those samples which indicate the presence of interference should be treated in one or more of the following ways:

1. Successively dilute and reanalyze the samples to eliminate interferences.

2. Modify the sample matrix either to remove interferences or to stabilize the analyte. Examples are the addition of ammonium nitrate to remove alkali chlorides and the addition of ammonium phosphate to retain cadmium. The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.

3. Analyze the sample by method of standard additions while noticing the precautions and limitations of its use (see Step 8.7.2).

3.2.2 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, use either background correction or choose an alternate wavelength. Background correction may also compensate for nonspecific broad-band absorption interference.

3.2.3 Continuum background correction cannot correct for all types of background interference. When the background interference cannot be compensated for, chemically remove the analyte or use an alternate form of background correction, e.g., Zeeman background correction.

3.2.4 Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analyte.

3.2.5 Samples containing large amounts of organic materials should be oxidized by conventional acid digestion before being placed in the furnace. In this way, broad-band absorption will be minimized.

3.2.6 Anion interference studies in the graphite furnace indicate that, under conditions other than isothermal, the nitrate anion is preferred. Therefore, nitric acid is preferable for any digestion or solubilization step. If another acid in addition to nitric acid is required, a minimum amount should be used. This applies particularly to hydrochloric and, to a lesser extent, to sulfuric and phosphoric acids.

3.2.7 Carbide formation resulting from the chemical environment of the furnace has been observed. Molybdenum may be cited as an example. When carbides form, the metal is released very slowly from the resulting metal carbide as atomization continues. Molybdenum may require 30 seconds or more atomization time before the signal returns to baseline levels. Carbide formation is greatly reduced and the sensitivity increased with the use of pyrolytically coated graphite. Elements that readily form carbides are noted with the symbol (p) in Table 1.

3.2.8 For comments on spectral interference, see Step 3.1.5.

3.2.9 Cross-contamination and contamination of the sample can be major sources of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in Step 4.8. Pipet tips are a frequent source of contamination. If suspected, they should be acid soaked with 1:5 nitric acid and rinsed thoroughly with tap and reagent water. The use of a better grade of pipet tip can greatly reduce this problem. Special attention should be given to reagent blanks in both analysis and in the correction of analytical results. Lastly, pyrolytic graphite, because of the production process and handling, can become contaminated. As many as five to ten high-temperature burns may be required to clean the tube before use.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer - Single- or dual-channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a graphical display.

4.2 Burner - The burner recommended by the particular instrument manufacturer should be used. For certain elements the nitrous oxide burner is required.

4.3 Hollow cathode lamps - Single-element lamps are preferred but multielement lamps may be used. Electrodeless discharge lamps may also be used when available. Other types of lamps meeting the performance criteria of this method may be used.

4.4 Graphite furnace - Any furnace device capable of reaching the specified temperatures is satisfactory.

4.5 Graphical display and recorder - A recorder is recommended for furnace work so that there will be a permanent record and that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, peak shape, etc., can be easily recognized.

4.6 Pipets - Microliter, with disposable tips. Sizes can range from 5 to 100 uL as required. Pipet tips should be checked as a possible source of contamination prior to their use. The accuracy of automatic pipets must be verified daily. Class A pipets can be used for the measurement of volumes larger than 1 mL.

4.7 Pressure-reducing valves - The supplies of fuel and oxidant should be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

4.8 Glassware - All glassware, polypropylene, or Teflon containers, including sample bottles, flasks and pipets, should be washed in the following sequence: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and reagent water. (Chromic acid should not be used as a cleaning agent for glassware if chromium is to be included in the analytical scheme.) If it can be documented through an active analytical quality control program using spiked samples and reagent blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first

ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. All reagents should be analyzed to provide proof that all constituents are below the MDLs.

5.2 Reagent water. All references to water in this method refer to reagent water unless otherwise specified. Reagent grade water will be of at least 16 Mega Ohm quality.

5.3 Nitric acid (concentrated), HNO_3. Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by adding the concentrated acid to an equal volume of water. If the reagent blank is less than the IDL, the acid may be used.

5.4 Hydrochloric acid (1:1), HCl. Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by adding the concentrated acid to an equal volume of water. If the reagent blank is less than the IDL, the acid may be used.

5.5 Fuel and oxidant - High purity acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or a cylinder of compressed air and should be clean and dry. Nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.

5.6 Stock standard metal solutions - Stock standard solutions are prepared from high purity metals, oxides, or nonhygroscopic salts using water and redistilled nitric or hydrochloric acids. (See individual methods for specific instructions.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1,000 mg of the metal per liter. Commercially available standard solutions may also be used. Where the sample viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) may be used (see Step 8.7).

5.7 Calibration standards - For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorbance of 0.0 to 0.7. Calibration standards are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time a batch of samples is analyzed. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range of the linear part of the curve. The calibration standards should be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following processing. Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution. Calibration standards for furnace procedures should be prepared as described on the individual sheets for that metal. Calibration curves are always required.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Metallic Analytes.

7.0 PROCEDURE

7.1 Preliminary treatment of waste water, ground water, EP extracts, and industrial waste is always necessary because of the complexity and variability of sample matrices. Solids, slurries, and suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Chapter Three, Step 3.2, Sample Preparation Methods. Samples which are to be analyzed for dissolved constituents need not be digested if they have been filtered and acidified.

7.2 Direct aspiration (flame) procedure

7.2.1 Differences between the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for a particular instrument. In general, after choosing the proper lamp for the analysis, allow the lamp to warm up for a minimum of 15 minutes, unless operated in a double-beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the current according to the manufacturer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant. Adjust the burner and nebulizer flow rate for maximum percent absorption and stability. Balance the photometer. Run a series of standards of the element under analysis. Construct a calibration curve by plotting the concentrations of the standards against absorbances. Set the curve corrector of a direct reading instrument to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. Standards must be run each time a sample or series of samples is run.

7.3 Furnace procedure

7.3.1 Furnace devices (flameless atomization) are a most useful means of extending detection limits. Because of differences between various makes and models of satisfactory instruments, no detailed operating instructions can be given for each instrument. Instead, the analyst should follow the instructions provided by the manufacturer of a particular instrument.

7.3.2 Background correction is important when using flameless atomization, especially below 350 nm. Certain samples, when atomized, may absorb or scatter light from the lamp. This can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high. Zeeman background correction is effective in overcoming composition or structured background

interferences. It is particularly useful when analyzing for As in the presence of Al and when analyzing for Se in the presence of Fe.

7.3.3 Memory effects occur when the analyte is not totally volatilized during atomization. This condition depends on several factors: volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization, and furnace design. This situation is detected through blank burns. The tube should be cleaned by operating the furnace at full power for the required time period, as needed, at regular intervals during the series of determinations.

7.3.4 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.3.5 To verify the absence of interference, follow the serial dilution procedure given in Step 8.6.

7.3.6 A check standard should be run after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. Tube life depends on sample matrix and atomization temperature. A conservative estimate would be that a tube will last at least 50 firings. A pyrolytic coating will extend that estimated life by a factor of three.

7.4 Calculation

7.4.1 For determination of metal concentration by direct aspiration and furnace: Read the metal value from the calibration curve or directly from the read-out system of the instrument.

7.4.2 If dilution of sample was required:

$$\text{ug/L metal in sample} = A \left(\frac{C + B}{C}\right)$$

where:

A = ug/L of metal in diluted aliquot from calibration curve.
B = Acid blank matrix used for dilution, mL.
C = Sample aliquot, mL.

7.4.3 For solid samples, report all concentrations in consistent units based on wet weight. Hence:

$$\text{ug metal/kg sample} = \frac{A \times V}{W}$$

where:

A = ug/L of metal in processed sample from calibration curve.
V = Final volume of the processed sample, mL.
W = Weight of sample, grams.

7.4.4 Different injection volumes must not be used for samples and standards. Instead, the sample should be diluted and the same size injection volume be used for both samples and standards. If dilution of the sample was required:

$$\text{ug/L of metal in sample} = Z \left(\frac{C + B}{C} \right)$$

where:

Z = ug/L of metal read from calibration curve or read-out system.
B = Acid blank matrix used for dilution mL.
C = Sample aliquot, mL.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 A calibration curve must be prepared each day with a minimum of a calibration blank and three standards. After calibration, the calibration curve must be verified by use of at least a calibration blank and a calibration check standard (made from a reference material or other independent standard material) at or near the mid-range. The calibration reference standard must be measured within 10 % of it's true value for the curve to be considered valid.

8.3 If more than 10 samples per day are analyzed, the working standard curve must be verified by measuring satisfactorily a mid-range standard or reference standard after every 10 samples. This sample value must be within 20% of the true value, or the previous ten samples need to be reanalyzed.

8.4 At least one matrix spike and one matrix spike duplicate sample shall be included in each analytical batch. A laboratory control sample shall also be processed with each sample batch. Refer to Chapter One for more information.

8.5 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) is recommended (see Section 8.7 below). Section 8.6 provides tests to evaluate the need for using the MSA.

8.6 Interference tests

8.6.1 Dilution test - For each analytical batch select one typical sample for serial dilution to determine whether interferences are present. The concentration of the analyte should be at least 25 times the estimated detection limit. Determine the apparent concentration in the undiluted sample. Dilute the sample by a minimum of five fold (1+4) and reanalyze. If all of the samples in the batch are below 10 times the detection limits, perform the spike recovery analysis described below. Agreement within 10% between the concentration for the undiluted sample and five times the concentration for the diluted sample indicates the absence of interferences, and such samples may be analyzed without using the method of standard additions.

8.6.2 Recovery test - If results from the dilution test do not agree, a matrix interference may be suspected and a spiked sample should be analyzed to help confirm the finding from the dilution test. Withdraw another aliquot of the test sample and add a known amount of analyte to bring the concentration of the analyte to 2 to 5 times the original concentration. If all of the samples in the batch have analyte concentrations below the detection limit, spike the selected sample at 20 times the detection limit. Analyze the spiked sample and calculate the spike recovery. If the recovery is less than 85% or greater than 115%, the method of standard additions shall be used for all samples in the batch.

8.7 Method of standard additions - The standard addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The method of standard additions shall be used for analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

8.7.1 The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_S of a standard analyte solution of concentration C_S. To the second aliquot (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration C_x is calculated:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B) V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

8.7.2 Improved results can be obtained by employing a series of standard additions. To equal volumes of the sample are added a series of standard solutions containing different known quantities of the analyte, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50 percent of the expected absorbance from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100 and 150 percent of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled

the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 1. A linear regression program may be used to obtain the intercept concentration.

8.7.3 For the results of this MSA technique to be valid, the following limitations must be taken into consideration:

1. The apparent concentrations from the calibration curve must be linear over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve. If the slope is significantly different (greater than 20%), caution should be exercised.

2. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

3. The determination must be free of spectral interference and corrected for nonspecific background interference.

8.8 All quality control measures described in Chapter One should be followed.

9.0 METHOD PERFORMANCE

9.1 See individual methods.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

TABLE 1.
ATOMIC ABSORPTION CONCENTRATION RANGES

Metal	Direct Aspiration		Furnace Procedure[a,c]
	Detection Limit (mg/L)	Sensitivity (mg/L)	Detection Limit (ug/L)
Aluminum	0.1	1	--
Antimony	0.2	0.5	3
Arsenic[b]	0.002	--	1
Barium	0.1	0.4	2
Beryllium	0.005	0.025	0.2
Cadmium	0.005	0.025	0.1
Calcium	0.01	0.08	--
Chromium	0.05	0.25	1
Cobalt	0.05	0.2	1
Copper	0.02	0.1	1
Iron	0.03	0.12	1
Lead	0.1	0.5	1
Lithium	0.002	0.04	--
Magnesium	0.001	0.007	--
Manganese	0.01	0.05	0.2
Mercury[d]	0.0002	--	--
Molybdenum(p)	0.1	0.4	1
Nickel	0.04	0.15	--
Osmium	0.03	1	--
Potassium	0.01	0.04	--
Selenium[b]	0.002	--	2
Silver	0.01	0.06	0.2
Sodium	0.002	0.015	--
Strontium	0.03	0.15	--
Thallium	0.1	0.5	1
Tin	0.8	4	--
Vanadium(p)	0.2	0.8	4
Zinc	0.005	0.02	0.05

NOTE: The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

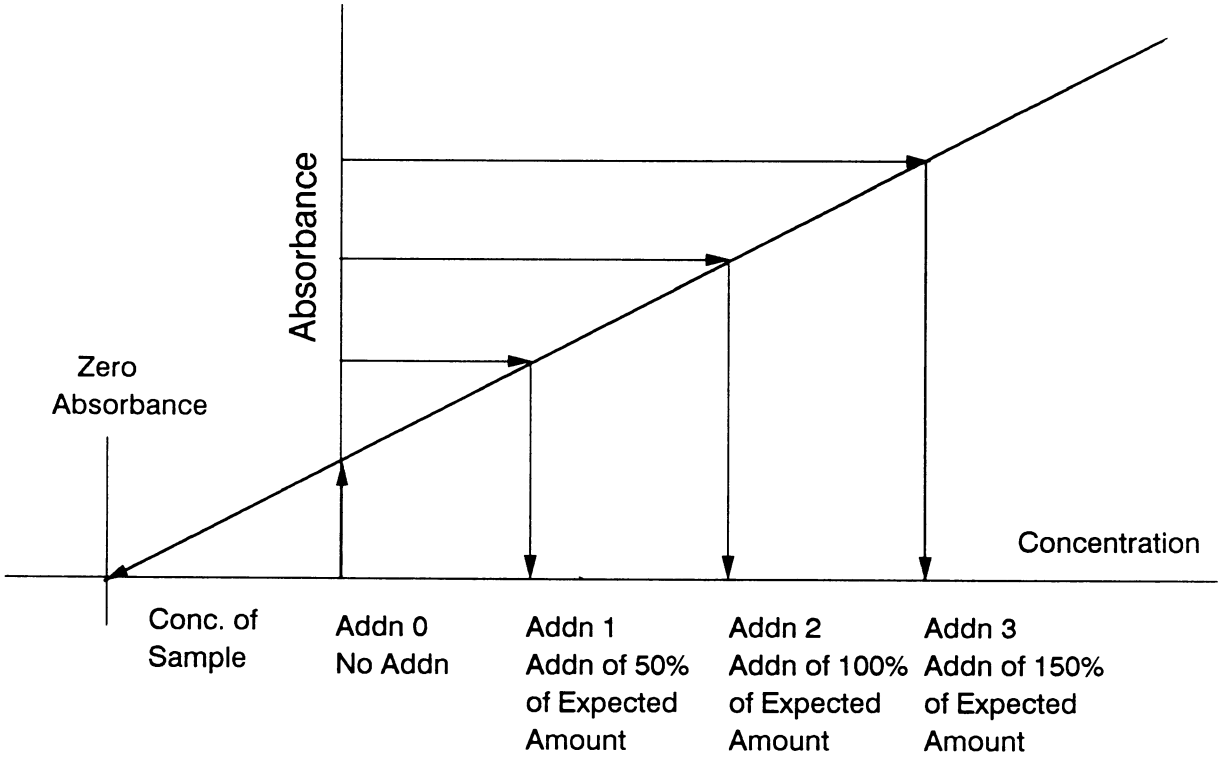
[a]For furnace sensitivity values, consult instrument operating manual.

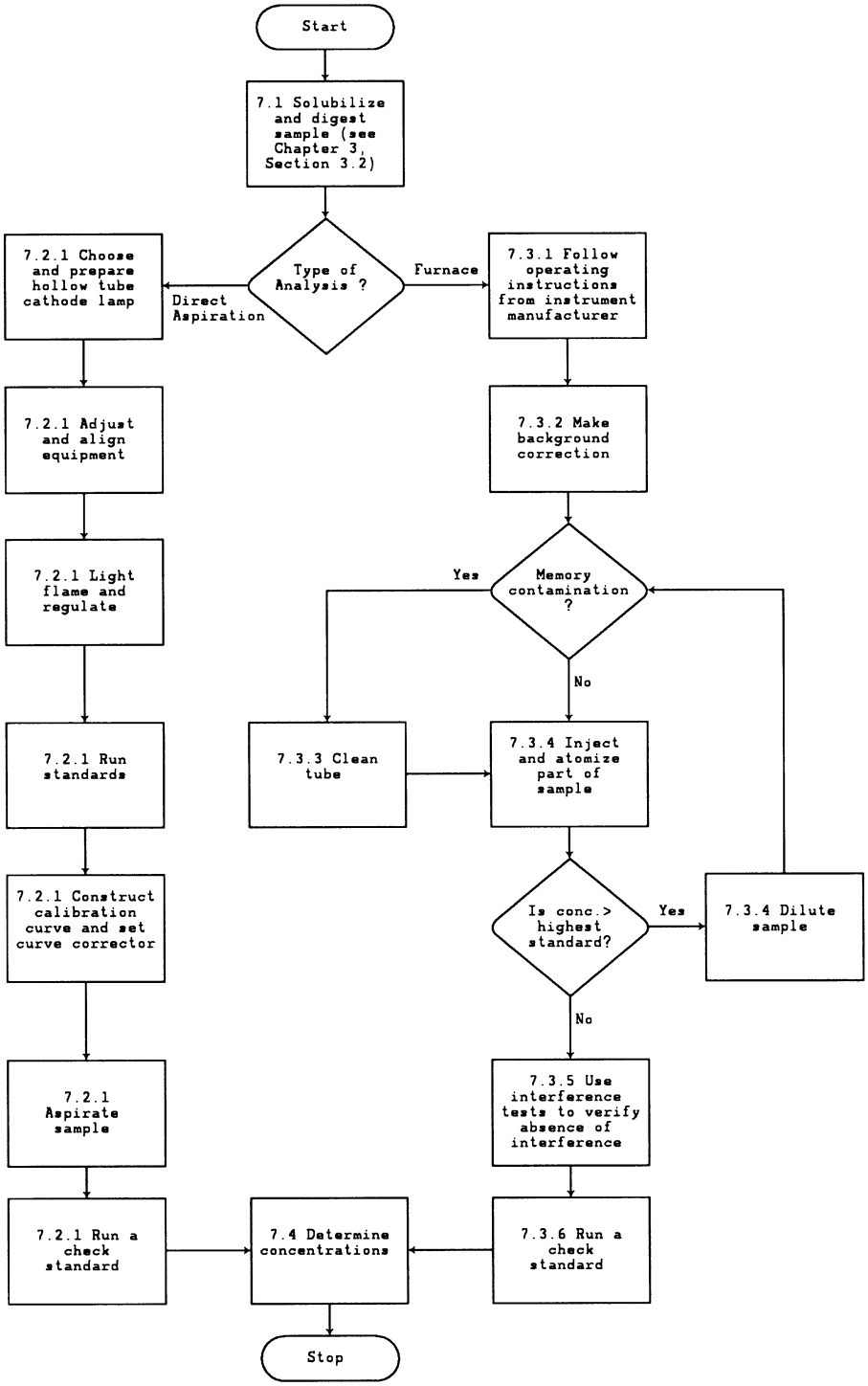
[b]Gaseous hydride method.

[c]The listed furnace values are those expected when using a 20-uL injection and normal gas flow, except in the cases of arsenic and selenium, where gas interrupt is used.

[d]Cold vapor technique.

FIGURE 1.
STANDARD ADDITION PLOT




Start
7.1 Solubilize and digest sample (see Chapter 3, Section 3.2)
Type of Analysis ?
Direct Aspiration
Furnace
7.2.1 Choose and prepare hollow tube cathode lamp
7.3.1 Follow operating instructions from instrument manufacturer
7.2.1 Adjust and align equipment
7.3.2 Make background correction
7.2.1 Light flame and regulate
Memory contamination ?
Yes
No
7.2.1 Run standards
7.3.3 Clean tube
7.3.4 Inject and atomize part of sample
7.2.1 Construct calibration curve and set curve corrector
Is conc.> highest standard?
Yes
7.3.4 Dilute sample
No
7.2.1 Aspirate sample
7.3.5 Use interference tests to verify absence of interference
7.2.1 Run a check standard
7.4 Determine concentrations
7.3.6 Run a check standard
Stop

Annex 2

الملحق الثـــانى

CHAPTER TWO

CHOOSING THE CORRECT PROCEDURE

SW-846 analytical methods are written as quantitative trace analytical methods to demonstrate that a waste does not contain analytes of concern that cause it to be managed as a hazardous waste. As such, these methods typically contain relatively stringent quality control (QC) criteria appropriate to trace analyses. However, if a particular application does not require data of this quality, less stringent QC criteria may be used. The purpose of this chapter is to aid the analyst in choosing the appropriate methods for sample analyses, based upon the sample matrix and the analytes to be determined. The ultimate responsibility for producing reliable analytical results lies with the entity subject to the regulation. Therefore, members of the regulated community are advised to refer to this chapter and to consult with knowledgeable laboratory personnel when choosing the most appropriate suite of analytical methods. In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements.

Section 2.1 provides guidance regarding the analytical flexibility inherent to SW-846 methods and the precedence of various QC criteria. Section 2.2 reviews the information required to choose the correct combination of methods for an analytical procedure. Section 2.3 provides useful information on implementing the method selection guidance for organic analyses. Section 2.4 provides guidance on characteristic analyses and Section 2.5 provides guidance on the determination of analytes in ground water.

2.1 GUIDANCE REGARDING FLEXIBILITY INHERENT TO SW-846 METHODS AND THE PRECEDENCE OF SW-846 QUALITY CONTROL CRITERIA

The specific products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency for use in the method. Glassware, reagents, supplies, equipment and settings other than those listed in this manual may be employed, provided that method performance appropriate for the intended RCRA application has been documented. Such performance includes consideration of precision, accuracy (or bias), recovery, representativeness, comparability, and sensitivity (detection, quantitation, or reporting limits) relative to the data quality objectives for the intended use of the analytical results. In response to this inherent flexibility, if an alternative analytical procedure is employed, then EPA expects the laboratory to demonstrate and document that the procedure is capable of providing appropriate performance for its intended application. This demonstration must not be performed after the fact, but as part of the laboratory's initial demonstration of proficiency with the method. The documentation should be in writing, maintained in the laboratory, and available for inspection upon request by authorized representatives of the appropriate regulatory authorities. The documentation should include the performance data as well as a detailed description of the procedural steps as performed (i.e., a written standard operating procedure).

Given this allowance for flexibility, EPA wishes to emphasize that this manual also contains procedures for "method-defined parameters," where the analytical result is wholly dependant on the process used to make the measurement. Examples include the use of the toxicity characteristic leaching procedure (TCLP) to prepare a leachate, and the flash point, pH, paint filter liquids, and corrosivity tests. In these instances, changes to the specific methods may change the end result

and incorrectly identify a waste as nonhazardous. Therefore, when the measurement of such method-defined parameters is required by regulation, those methods are not subject to the flexibility afforded in other methods.

Analysts and data users are advised that even for those analytes that are not method-defined, different procedures may produce some difference in results. Common examples include the differences in recoveries of phenolic compounds extracted from water by separatory funnel (Method 3510) and continuous liquid-liquid (Method 3520) extraction techniques, differences in recoveries of many compounds between Soxhlet (Method 3540) and ultrasonic (Method 3550) extraction techniques, and differences resulting from the choice of acid digestion of metals (Method 3050) or microwave digestion (Method 3051). Where practical, the Agency has included guidance in the individual methods regarding known potential problems, and analysts are advised to review this information carefully in choosing or modifying analytical procedures. Chapter One describes a variety of QC procedures that may be used to evaluate the quality of the analytical results. Additional QC procedures may be described in the individual methods. The results of these QC procedures should be used by the analyst to evaluate if the choice of the analytical procedures and/or any modifications are appropriate to generate data of the quality necessary to satisfy the data quality needs of the intended application.

The performance data included in the SW-846 methods are not intended to be used as absolute QC acceptance criteria for method performance. The data are intended to be guidance, by providing typical method performance in typical matrices, to assist the analyst in selection of the appropriate method for the intended application. In addition, it is the responsibility of the laboratory to establish actual operating parameters and in-house QC acceptance criteria, based on its own laboratory SOPs and in-house QC program, to demonstrate appropriate performance of the methods used in that laboratory for the RCRA analytical applications for which they are intended.

The regulated community is further advised that the methods here or from other sources need only be used for those specific analytes of concern that are subject to regulation or other monitoring requirements. The fact that a method provides a long list of analytes does not mean that each of those analytes is subject to any or all regulations, or that all of those analytes must be analyzed each time the method is employed, or that all of the analytes can be analyzed using a single sample preparation procedure. It is EPA's intention that the target analyte list for any procedure includes those analytes necessary to meet the data quality objectives of the project, i.e., those analytes subject to monitoring requirements and set out in a RCRA permit (or other applicable regulation), plus those analytes used in the methods for QC purposes, such as surrogates, internal standards, system performance check compounds, etc. Additional analytes, not included on the analyte list of a particular method(s) but needed for a specific project, may be analyzed by that particular method(s), if appropriate performance can be demonstrated for the analytes of concern in the matrices of concern at the levels of concern.

2.1.1 Trace Analysis vs. Macroanalysis

Through the choice of sample size and concentration procedures, the methods presented in SW-846 were designed to address the problem of "trace" analyses (<1000 ppm), and have been developed for an optimized working range. These methods are also applicable to "minor" (1000 ppm - 10,000 ppm) and "major" (>10,000 ppm) analyses, as well, through use of appropriate sample preparation techniques that result in analyte concentrations within that optimized range. Such sample preparation techniques include:

1) adjustment of size of sample prepared for analysis (for homogeneous samples),
2) adjustment of injection volumes,
3) dilution or concentration of sample,
4) elimination of concentration steps prescribed for "trace" analyses, and
5) direct injection (of samples to be analyzed for volatile constituents).

The performance data presented in each of these methods were generated from "trace" analyses, and may not be applicable to "minor" and "major" analyses. Generally, extraction efficiency improves as concentration increases.

CAUTION: Great care should be taken when performing trace analyses after the analysis of concentrated samples, given the possibility of contamination.

2.1.2 Choice of Apparatus and Preparation of Reagents

Since many types and sizes of glassware and supplies are commercially available, and since it is possible to prepare reagents and standards in many different ways, the apparatus, reagents, and volumes specified in these methods may be replaced by any similar types as long as this substitution does not affect the overall quality of the analyses.

2.1.3 Quality Control Criteria Precedence

Chapter One contains general quality control (QC) guidance for analyses using SW-846 methods. QC guidance specific to a given analytical technique (e.g., extraction, cleanup, sample introduction, or analysis) may be found in Methods 3500, 3600, 5000, 7000, and 8000. Method-specific QC criteria may be found in Sec. 8.0 of each individual method (or in Sec. 11.0 of air sampling methods). When inconsistencies exist between the information in these locations, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One.

2.2 REQUIRED INFORMATION

In order to choose the correct combination of methods to comprise the appropriate analytical procedure, some basic information is required.

2.2.1 Physical State(s) of Sample

The phase characteristics of the sample must be known. There are several general categories of phases into which the sample may be categorized, including:

Aqueous
Sludge
TCLP or EP Extract
Solid
Ground Water
Oil or other Organic Liquid
Stack Sampling (VOST) Condensate
Multiphase Sample

There may be a substantial degree of overlap between the phases listed above and it may be useful to further divide these phases in certain instances. A multiphase sample may be a

combination of aqueous, organic liquid, sludge, and/or solid phases, and generally must undergo a phase separation as the first step in the analytical procedure.

2.2.2 Analytes

Analytes may be divided into various classes based on the determinative methods which are used to identify and quantify them. The most basic differentiation is between organic (e.g., carbon-containing) analytes and inorganic (e.g., metals and anions) analytes.

Table 2-1 is an alphabetical list of analytes cited within the SW-846 organic determinative methods. These analytes have been evaluated by those methods. The methods may also be applicable to other analytes that are similar to those listed. Tables 2-2A and 2-2B list the organic analytes that may be prepared using Method 3650. Table 2-3 lists the organic analytes that are collected from stack gas effluents using the volatile organic sampling train (VOST) methodology. Tables 2-4 through 2-34 list the analytes by organic determinative method.

Table 2-35 indicates which methods are applicable to inorganic analytes.

2.2.3 Detection Limits

Some regulations may require a specific sensitivity or detection limit for an analysis, as in the determination of analytes for the Toxicity Characteristic (TC). Drinking water detection limits, for those specific organic and metallic analytes covered by the National Primary Drinking Water Regulations, are desired in the analysis of ground water.

2.2.4 Analytical Objective

Knowledge of the analytical objective will be useful in the choice of sample preparation procedures and in the selection of a determinative method. This is especially true when the sample has more than one phase. Knowledge of the analytical objective may not be possible or desirable at all management levels, but that information should be transmitted to the analytical laboratory management to ensure that the correct techniques are used during the analytical effort.

2.2.5 Detection and Monitoring

The strategy for detection of compounds in environmental or process samples may be contrasted with the strategy for collecting monitoring data. Detection samples define initial conditions. When there is little information available about the composition of the sample source, e.g., a well or process stream, mass spectral identification of organic analytes leads to fewer false positive results. Thus, the most practical form of detection for organic analytes is often mass spectral identification. However, where the sensitivity requirements exceed those that can be achieved using mass spectral method (e.g., GC/MS or HPLC/MS), it may be necessary to employ a more sensitive detection method (e.g., electron capture). In these instances, the risk of false positive results may be minimized by confirming the results through a second analysis with a dissimilar detector or chromatographic column. Thus, the choice of technique for organic analytes may be governed by the detection limit requirements and potential interferants.

Similarly, the choice of technique for metals is governed by the detection limit requirements and potential interferants.

In contrast, monitoring samples are analyzed to confirm existing and on-going conditions, tracking the presence or absence of known constituents in an environmental or process matrix. In well-defined matrices and under stable analytical conditions, less compound-specific detection modes may be used, as the risk of false positive results is less.

2.2.6 Sample Containers, Preservations, and Holding Times

Appropriate sample containers, sample preservation techniques, and sample holding times for aqueous matrices are listed in Table 2-36, near the end of this chapter. Similar information may be found in Table 3-1 of Chapter Three (inorganic analytes) and Table 4-1 of Chapter Four (organic analytes). Samples must be extracted and analyzed within the specified holding times for the results to be considered reflective of total concentrations. Analytical data generated outside of the specified holding times must be considered to be minimum values only. Such data may be used to demonstrate that a waste is hazardous where it shows the concentration of a constituent to be above the regulatory threshold but cannot be used to demonstrate that a waste is not hazardous.

2.3 IMPLEMENTING THE GUIDANCE

The choice of the appropriate sequence of methods depends on the information required and on the experience of the analyst. Figure 2-1 summarizes the organic analysis options available. Appropriate selection is confirmed by the quality control results. The use of the recommended procedures, whether they are approved or mandatory, does not release the analyst from demonstrating the correct execution of the method.

2.3.1 Extraction and Sample Preparation Procedures for Organic Analytes

Methods for preparing samples for organic analytes are shown in Table 2-37. Method 3500 and associated methods should be consulted for further details on preparing the sample for analysis.

2.3.1.1 Aqueous Samples

Methods 3510 and 3520 may be used for extraction of the semivolatile organic compounds from aqueous samples. The choice of a preparative method depends on the sample. Method 3510, a separatory funnel liquid-liquid extraction technique, is appropriate for samples which will not form a persistent emulsion interface between the sample and the extraction solvent. The formation of an emulsion that cannot be broken up by mechanical techniques will prevent proper extraction of the sample. Method 3520, a continuous liquid-liquid extraction technique, may be used for any aqueous sample and will minimize emulsion formation.

Method 3535 is solid-phase extraction technique that has been tested for organochlorine pesticides and phthalate esters and may be applicable to other semivolatile and extractable compounds as well. The aqueous sample is passed through a solid sorbent material which traps the analytes. They are then eluted from the solid-phase sorbent with a small volume of organic solvent. This technique may be used to minimize the volumes of organic solvents that are employed, but may not be appropriate for aqueous samples with high suspended solids contents.

2.3.1.1.1 Basic or Neutral Extraction of Semivolatile Analytes

The solvent extract obtained by performing Method 3510, 3520, or 3535 at a neutral or basic pH will contain the neutral organic compounds and the organic bases of interest. Refer to Table 1 in the extraction methods (3510 and/or 3520) for guidance on the requirements for pH adjustment prior to extraction and analysis.

2.3.1.1.2 Acidic Extraction of Phenols and Acid Analytes

The solvent extract obtained by performing Method 3510, 3520, or 3535 at a pH less than or equal to 2 will contain the phenols and acid extractable organics of interest.

2.3.1.2 Solid Samples

Soxhlet extraction (Methods 3540 and 3541), ultrasonic extraction (Method 3550), and accelerated solvent extraction (Method 3545) may be used with solid samples. Consolidated samples should be ground finely enough to pass through a 1 mm sieve. In limited applications, waste dilution (Methods 3580 and 3585) may be used if the entire sample is soluble in the specified solvent.

Methods 3540, 3541, 3545, and 3550 are neutral-pH extraction techniques and therefore, depending on the analysis requirements, acid-base partition cleanup (Method 3650) may be necessary. Method 3650 will only be needed if chromatographic interferences are severe enough to prevent detection of the analytes of interest. This separation will be most important if a GC method is chosen for analysis of the sample. If GC/MS is used, the ion selectivity of the technique may compensate for chromatographic interferences.

There are two extraction procedures for solid samples that employ supercritical fluid extraction (SFE). Method 3560 is a technique for the extraction of petroleum hydrocarbons from various solid matrices using carbon dioxide at elevated temperature and pressure. Method 3561 may be used to extract polynuclear aromatic hydrocarbons (PAHs) from solid matrices using supercritical carbon dioxide.

2.3.1.3 Oils and Organic Liquids

Method 3580, waste dilution, may be used to prepare oils and organic liquid samples for analysis of semivolatile and extractable organic analytes by GC or GC/MS. Method 3585 may be employed for the preparation of these matrices for volatiles analysis by GC or GC/MS. To avoid overloading the analytical detection system, care must be exercised to ensure that proper dilutions are made. Methods 3580 and 3585 give guidance on performing waste dilutions.

To remove interferences for semivolatiles and extractables, Method 3611 (Alumina cleanup) may be performed on an oil sample directly, without prior sample preparation.

Method 3650 is the only other preparative procedure for oils and other organic liquids. This procedure is a back extraction into an aqueous phase. It is generally introduced as a cleanup procedure for extracts rather than as a preparative procedure. Oils generally have

a high concentration of semivolatile compounds and, therefore, preparation by Method 3650 should be done on a relatively small aliquot of the sample. Generally, extraction of 1 mL of oil will be sufficient to obtain a saturated aqueous phase and avoid emulsions.

2.3.1.4 Sludge Samples

Determining the appropriate methods for analysis of sludges is complicated because of the lack of precise definitions of sludges with respect to the relative percent of liquid and solid components. There is no set ratio of liquid to solid which enables the analyst to determine which of the three extraction methods cited is the most appropriate. Sludges may be classified into three categories: liquid sludges, solid sludges, and emulsions, but with appreciable overlap.

If the sample is an organic sludge (solid material and organic liquid, as opposed to an aqueous sludge), the sample should be handled as a multiphase sample.

2.3.1.4.1 Liquid Sludges

Use of Method 3510 or Method 3520 may be applicable to sludges that behave like and have the consistency of aqueous liquids. Ultrasonic extraction (Method 3550) and Soxhlet (Method 3540) procedures will, most likely, be ineffective because of the overwhelming presence of the liquid aqueous phase.

2.3.1.4.2 Solid Sludges

Soxhlet extraction (Methods 3540 and 3541), accelerated solvent (Method 3545) extraction, and ultrasonic extraction (Method 3550) will be more effective when applied to sludge samples that resemble solids. Samples may be dried or centrifuged to form solid materials for subsequent determination of semivolatile compounds.

Using Method 3650, Acid-Base Partition Cleanup, on the extract may be necessary, depending on whether chromatographic interferences prevent determination of the analytes of interest.

2.3.1.4.3 Emulsions

Attempts should be made to break up and separate the phases of an emulsion. Several techniques are effective in breaking emulsions or separating the phases of emulsions, including:

1. Freezing/thawing: Certain emulsions will separate if exposed to temperatures below 0°C.

2. Salting out: Addition of a salt to make the aqueous phase of an emulsion too polar to support a less polar phase promotes separation.

3. Centrifugation: Centrifugal force may separate emulsion components by density.

4. Addition of water or ethanol: Emulsion polymers may be destabilized when a preponderance of the aqueous phase is added.

5. Forced filtering through glass wool: Many emulsions can be broken by forcing the emulsion through a pad of Pyrex glass wool in a drying column using a slight amount of air pressure (using a rubber bulb usually provides sufficient pressure).

If techniques for breaking emulsions fail, use Method 3520. If the emulsion can be broken, the different phases (aqueous, solid, or organic liquid) may then be analyzed separately.

2.3.1.5 Multiphase Samples

Choice of the procedure for separating multiphase samples is highly dependent on the objective of the analysis. With a sample in which some of the phases tend to separate rapidly, the percent weight or volume of each phase should be calculated and each phase should be individually analyzed for the required analytes.

An alternate approach is to obtain a homogeneous sample and attempt a single analysis on the combination of phases. This approach will give no information on the abundance of the analytes in the individual phases other than what can be implied by solubility.

A third alternative is to select phases of interest and to analyze only those selected phases. This tactic must be consistent with the sampling/analysis objectives or it will yield insufficient information for the time and resources expended. The phases selected should be compared with Figure 2-1 and Table 2-37 for further guidance.

2.3.2 Cleanup Procedures

Each category in Table 2-38, Cleanup of Organic Analyte Extracts, corresponds to one of the possible determinative methods available in the manual. Cleanups employed are determined by the analytes of interest within the extract. However, the necessity of performing cleanup may also depend upon the matrix from which the extract was developed. Cleanup of a sample may be done exactly as instructed in the cleanup method for some of the analytes. There are some instances when cleanup using one of the methods may only proceed after the procedure is modified to optimize recovery and separation. Several cleanup techniques may be possible for each analyte category. The information provided is not meant to imply that any or all of these methods must be used for the analysis to be acceptable. Extracts with components which interfere with spectral or chromatographic determinations are expected to be subjected to cleanup procedures.

The analyst's discretion must determine the necessity for cleanup procedures, as there are no clear cut criteria for indicating their use. Method 3600 and associated methods should be consulted for further details on extract cleanup.

2.3.3 Determinative Procedures

The determinative methods for organic analytes have been divided into three categories, as shown in Table 2-39: gas chromatography/mass spectrometry (GC/MS); specific detection methods, i.e., gas chromatography (GC) with specific non-MS detectors; and high performance liquid chromatography (HPLC). This division is intended to help an analyst choose which determinative method will apply. Under each analyte column, SW-846 method numbers have been indicated, if appropriate, for the determination of the analyte. A blank has been left if no chromatographic determinative method is available.

Generally, the MS procedures are more specific but less sensitive than the appropriate gas chromatographic/specific detection method.

Method 8000 gives a general description of the techniques of gas chromatography and high performance liquid chromatography. Method 8000 should be consulted prior to application of any of the gas chromatographic methods.

Method 8081 (organochlorine pesticides), Method 8082 (polychlorinated biphenyls), Method 8141 (organophosphorus pesticides), and Method 8151 (chlorinated herbicides), are preferred over GC/MS because of the combination of selectivity and sensitivity of the flame photometric, nitrogen-phosphorus, and electron capture detectors.

Method 8260 is a GC/MS method for volatile analytes, which employs a capillary column. A variety of sample introduction techniques may be used with Method 8260, including Methods 5021, 5030, 5031, 5035, and 3585. A GC with a selective detector is also useful for the determination of volatile organic compounds in a monitoring scenario, as described in Sec. 2.2.5.

Method 8270 is a GC/MS method for semivolatile analytes, which employs a capillary column.

Table 2-39 lists several GC and HPLC methods that apply to only a small number of analytes. Methods 8031 and 8033 are GC methods for acrolein, acrylonitrile, and acetonitrile. Methods 8315 and 8316 are HPLC methods for these three analytes. Method 8316 also addresses acrylamide, which may be analyzed by Method 8032.

HPLC methods have been developed for other types of analytes, most notably carbamates (Method 8318); azo dyes, phenoxy acid herbicides, carbamates, and organophosphorus pesticides (Method 8321); PAHs (Method 8310); explosives (Methods 8330, 8331, and 8332); and some volatile organics (Methods 8315 and 8316).

Method 8430 utilizes a Fourier Transform Infrared Spectrometer (FT-IR) coupled to a gas chromatograph to determine bis(2-chloroethyl) ether and its hydrolysis products. The sample is introduced by direct aqueous injection. Method 8440 may be employed for the determination of total recoverable petroleum hydrocarbons (TRPH) in solid samples by infrared (IR) spectrophotometry. The samples may be extracted with supercritical carbon dioxide, using Method 3560.

2.4 CHARACTERISTICS

Figure 2-2 outlines a sequence for determining if a waste exhibits one or more of the characteristics of a hazardous waste.

2.4.1 EP and TCLP extracts

The leachate obtained from using either the EP (Figure 2-3A) or the TCLP (Figure 2-3B) is an aqueous sample, and therefore, requires further solvent extraction prior to the analysis of semivolatile compounds.

The TCLP leachate is solvent extracted with methylene chloride at a pH > 11 and at a pH <2 by either Method 3510 or 3520. Method 3510 should be used unless the formation of emulsions between the sample and the solvent prevent proper extraction. If this problem is encountered, Method 3520 should be employed.

The solvent extract obtained by performing either Method 3510 or 3520 at a basic or neutral pH will contain the base/neutral compounds of interest. Refer to the specific determinative method for guidance on the pH requirements for extraction prior to analysis. Method 5031 (Azeotropic Distillation) may be used as an effective preparative method for pyridine.

Due to the high concentration of acetate in the TCLP extract, it is recommended that purge-and-trap be used to introduce the volatile sample into the gas chromatograph.

2.5 GROUND WATER

Appropriate analysis schemes for the determination of analytes in ground water are presented in Figures 2-4A, 2-4B, and 2-4C. Quantitation limits for the inorganic analytes should correspond to the drinking water limits which are available.

2.5.1 Special Techniques for Inorganic Analytes

All atomic absorption analyses should employ appropriate background correction systems whenever spectral interferences could be present. Several background correction techniques are employed in modern atomic absorption spectrometers. Matrix modification can complement background correction in some cases. Since no approach to interference correction is completely effective in all cases, the analyst should attempt to verify the adequacy of correction. If the interferant is known (e.g., high concentrations of iron in the determination of selenium), accurate analyses of synthetic solutions of the interferant (with and without analyte) could establish the efficacy of the background correction. If the nature of the interferant is not established, good agreement of analytical results using two substantially different wavelengths could substantiate the adequacy of the background correction.

To reduce matrix interferences, all graphite furnace atomic absorption (GFAA) analyses should be performed using techniques which maximize an isothermal environment within the furnace cell. Data indicate that two such techniques, L'vov platform and the Delayed Atomization Cuvette (DAC), are equivalent in this respect, and produce high quality results.

All furnace atomic absorption analysis should be carried out using the best matrix modifier for the analysis. Some examples of modifiers are listed below. (See also the appropriate methods.)

Element(s)	Modifier(s)
As and Se	Nickel nitrate, palladium
Pb	Phosphoric acid, ammonium phosphate, palladium
Cd	Ammonium phosphate, palladium
Sb	Ammonium nitrate, palladium
Tl	Platinum, palladium

The ICP calibration standards must match the acid composition and strength of the acids contained in the samples. Acid strengths in the ICP calibration standards should be stated in the raw data. When using a method which permits the use of internal standardization, and the internal standardization option is being used, matrix matching is not required.

2.6 REFERENCES

1. Barcelona, M.J. "TOC Determinations in Ground Water"; Ground Water 1984, 22(1), 18-24.

2. Riggin, R.; et al. Development and Evaluation of Methods for Total Organic Halide and Purgeable Organic Halide in Wastewater; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1984; EPA-600/4-84-008.

3. McKee, G.; et al. Determination of Inorganic Anions in Water by Ion Chromatography; (Technical addition to Methods for Chemical Analysis of Water and Wastewater, EPA 600/4-79-020), U.S. Environmental Protection Agency. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1984; EPA-600/4-84-017.

TABLE 2-1
DETERMINATIVE METHODS FOR ORGANIC ANALYTES

Analyte	Applicable Method(s)
Acenaphthene	8100, 8270, 8275, 8310, 8410
Acenaphthylene	8100, 8270, 8275, 8310, 8410
Acetaldehyde	8315
Acetone	8015, 8260, 8315
Acetonitrile	8015, 8033, 8260
Acetophenone	8270
2-Acetylaminofluorene	8270
1-Acetyl-2-thiourea	8270
Acifluorfen	8151
Acrolein (Propenal)	8015, 8260, 8315, 8316
Acrylamide	8032, 8316
Acrylonitrile	8015, 8031, 8260, 8316
Alachlor	8081
Aldicarb (Temik)	8318, 8321
Aldicarb sulfone	8318, 8321
Aldicarb sulfoxide	8321
Aldrin	8081, 8270
Allyl alcohol	8015, 8260
Allyl chloride	8021, 8260
2-Aminoanthraquinone	8270
Aminoazobenzene	8270
4-Aminobiphenyl	8270
Aminocarb	8321
2-Amino-4,6-dinitrotoluene (2-Am-DNT)	8330
4-Amino-2,6-dinitrotoluene (4-Am-DNT)	8330
3-Amino-9-ethylcarbazole	8270
Anilazine	8270
Aniline	8131, 8270
o-Anisidine	8270
Anthracene	8100, 8270, 8275, 8310, 8410
Aramite	8270
Aroclor-1016 (PCB-1016)	8082, 8270
Aroclor-1221 (PCB-1221)	8082, 8270
Aroclor-1232 (PCB-1232)	8082, 8270
Aroclor-1242 (PCB-1242)	8082, 8270
Aroclor-1248 (PCB-1248)	8082, 8270
Aroclor-1254 (PCB-1254)	8082, 8270
Aroclor-1260 (PCB-1260)	8082, 8270
Aspon	8141
Asulam	8321
Atrazine	8141
Azinphos-ethyl	8141
Azinphos-methyl	8141, 8270
Barban	8270, 8321
Baygon (Propoxur)	8318, 8321
Bendiocarb	8321

Analyte	Applicable Method(s)
Benefin	8091
Benomyl	8321
Bentazon	8151
Benzal chloride	8121
Benzaldehyde	8315
Benz(a)anthracene	8100, 8270, 8275, 8310, 8410
Benzene	8021, 8260
Benzenethiol (Thiophenol)	8270
Benzidine	8270, 8325
Benzo(b)fluoranthene	8100, 8270, 8275, 8310
Benzo(j)fluoranthene	8100
Benzo(k)fluoranthene	8100, 8270, 8275, 8310
Benzoic acid	8270, 8410
Benzo(g,h,i)perylene	8100, 8270, 8275, 8310
Benzo(a)pyrene	8100, 8270, 8275, 8310, 8410
p-Benzoquinone	8270
Benzotrichloride	8121
Benzoylprop ethyl	8325
Benzyl alcohol	8270
Benzyl benzoate	8061
Benzyl chloride	8021, 8121, 8260
α-BHC (α-Hexachlorocyclohexane)	8081, 8121, 8270
β-BHC (β-Hexachlorocyclohexane)	8081, 8121, 8270
δ-BHC (δ-Hexachlorocyclohexane)	8081, 8121, 8270
γ-BHC (Lindane, γ-Hexachlorocyclohexane)	8081, 8121, 8270
Bis(2-chloroethoxy)methane	8111, 8270, 8410
Bis(2-chloroethyl) ether	8111, 8270, 8410, 8430
Bis(2-chloroethyl)sulfide	8260
Bis(2-chloroisopropyl) ether	8021, 8111, 8270, 8410
Bis(2-n-butoxyethyl) phthalate	8061
Bis(2-ethoxyethyl) phthalate	8061
Bis(2-ethylhexyl) phthalate	8061, 8270, 8410
Bis(2-methoxyethyl) phthalate	8061
Bis(4-methyl-2-pentyl)-phthalate	8061
Bolstar (Sulprofos)	8141
Bromacil	8321
Bromoacetone	8021, 8260
4-Bromoaniline	8131
Bromobenzene	8021, 8260
Bromochloromethane	8021, 8260
2-Bromo-6-chloro-4-nitroaniline	8131
Bromodichloromethane	8021, 8260
2-Bromo-4,6-dinitroaniline	8131
4-Bromofluorobenzene	8260
Bromoform	8021, 8260
Bromomethane	8021, 8260

TABLE 2-1. (Continued)

Analyte	Applicable Method(s)
4-Bromophenyl phenyl ether	8111, 8270, 8275, 8410
Bromoxynil	8270
Butanal	8315
1-Butanol (n-Butyl alcohol)	8015
n-Butanol	8260
2-Butanone (Methyl ethyl ketone, MEK)	8015, 8260
Butralin	8091
n-Butyl alcohol (1-Butanol)	8015
t-Butyl alcohol	8015
n-Butylbenzene	8021, 8260
sec-Butylbenzene	8021, 8260
tert-Butylbenzene	8021, 8260
Butyl benzyl phthalate	8061, 8270, 8410
2-sec-Butyl-4,6-dinitrophenol (DNBP, Dinoseb)	8041, 8151, 8270, 8321
Caffeine	8321
Captafol	8081, 8270
Captan	8270
Carbaryl (Sevin)	8270, 8318, 8321, 8325
Carbendazim	8321
Carbofuran (Furaden)	8270, 8318, 8321
Carbon disulfide	8260
Carbon tetrachloride	8021, 8260
Carbophenothion	8141, 8270
Chloral hydrate	8260
Chloramben	8151
Chlordane (NOS)	8270
α-Chlordane	8081
γ-Chlordane	8081
Chlorfenvinphos	8141, 8270
Chloroacetonitrile	8260
2-Chloroacrylonitrile	8015
2-Chloroaniline	8131
3-Chloroaniline	8131
4-Chloroaniline	8131, 8270, 8410
Chlorobenzene	8021, 8260
Chlorobenzilate	8081, 8270
2-Chlorobiphenyl	8082, 8275
2-Chloro-1,3-butadiene (Chloroprene)	8021, 8260
1-Chlorobutane	8260
Chlorodibromomethane (Dibromochloromethane)	8021, 8260
2-Chloro-4,6-dinitroaniline	8131
1-Chloro-2,4-dinitrobenzene	8091
1-Chloro-3,4-dinitrobenzene	8091
Chloroethane	8021, 8260
2-Chloroethanol	8021, 8260, 8430
2-(2-Chloroethoxy)ethanol	8430

Analyte	Applicable Method(s)
2-Chloroethyl vinyl ether	8021, 8260
Chloroform	8021, 8260
1-Chlorohexane	8260
Chloromethane	8021, 8260
5-Chloro-2-methylaniline	8270
Chloromethyl methyl ether	8021
2-Chloro-5-methylphenol	8041
4-Chloro-2-methylphenol	8041
4-Chloro-3-methylphenol	8041, 8270, 8410
3-(Chloromethyl)pyridine hydrochloride	8270
1-Chloronaphthalene	8270, 8275
2-Chloronaphthalene	8121, 8270, 8410
Chloroneb	8081
2-Chloro-4-nitroaniline	8131
4-Chloro-2-nitroaniline	8131
1-Chloro-2-nitrobenzene	8091
1-Chloro-4-nitrobenzene	8091
2-Chloro-6-nitrotoluene	8091
4-Chloro-2-nitrotoluene	8091
4-Chloro-3-nitrotoluene	8091
2-Chlorophenol	8041, 8270, 8410
3-Chlorophenol	8041
4-Chlorophenol	8041, 8410
4-Chloro-1,2-phenylenediamine	8270
4-Chloro-1,3-phenylenediamine	8270
4-Chlorophenyl phenyl ether	8111, 8270, 8410
2-Chlorophenyl 4-nitrophenyl ether	8111
3-Chlorophenyl 4-nitrophenyl ether	8111
4-Chlorophenyl 4-nitrophenyl ether	8111
o-Chlorophenyl thiourea	8325
Chloroprene (2-Chloro-1,3-butadiene)	8021, 8260
3-Chloropropionitrile	8260
Chloropropham	8321
Chloropropylate	8081
Chlorothalonil	8081
2-Chlorotoluene	8021, 8260
4-Chlorotoluene	8021, 8260
Chloroxuron	8321
Chlorpyrifos	8141
Chlorpyrifos methyl	8141
Chrysene	8100, 8270, 8275, 8310, 8410
Coumaphos	8141, 8270
Coumarin Dyes	8321
p-Cresidine	8270
o-Cresol (2-Methylphenol)	8041, 8270, 8410
m-Cresol (3-Methylphenol)	8041, 8270

TABLE 2-1. (Continued)

Analyte	Applicable Method(s)
p-Cresol (4-Methylphenol)	8041, 8270, 8275, 8410
Crotonaldehyde	8015, 8260, 8315
Crotoxyphos	8141, 8270
Cyclohexanone	8315
2-Cyclohexyl-4,6-dinitrophenol	8041, 8270
2,4-D	8151, 8321
Dalapon	8151, 8321
2,4-DB	8151, 8321
DBCP (1,2-Dibromo-3-chloropropane)	8011, 8021, 8081, 8260, 8270
2,4-D, butoxyethanol ester	8321
DCM (Dichloromethane, Methylene chloride)	8021, 8260
DCPA	8081
DCPA diacid	8151
4,4'-DDD	8081, 8270
4,4'-DDE	8081, 8270
4,4'-DDT	8081, 8270
DDVP (Dichlorvos, Dichlorovos)	8141, 8270, 8321
2,2',3,3'4,4'5,5',6,6'-Decachlorobiphenyl	8275
Decanal	8315
Demeton-O, and Demeton-S	8141, 8270
2,4-D, ethylhexyl ester	8321
Diallate	8081, 8270
Diamyl phthalate	8061
2,4-Diaminotoluene	8270
Diazinon	8141
Dibenz(a,h)acridine	8100
Dibenz(a,j)acridine	8100, 8270
Dibenz(a,h)anthracene	8100, 8270, 8275, 8310
7H-Dibenzo(c,g)carbazole	8100
Dibenzofuran	8270, 8275, 8410
Dibenzo(a,e)pyrene	8100, 8270
Dibenzo(a,h)pyrene	8100
Dibenzo(a,i)pyrene	8100
Dibenzothiophene	8275
Dibromochloromethane (Chlorodibromomethane)	8021, 8260
1,2-Dibromo-3-chloropropane (DBCP)	8011, 8260, 8270
1,2-Dibromoethane (EDB, Ethylene dibromide)	8011, 8021, 8260
Dibromofluoromethane	8260
Dibromomethane	8021, 8260
2,6-Dibromo-4-nitroaniline	8131
2,4-Dibromophenyl 4-nitrophenyl ether	8111
Di-n-butyl phthalate	8061, 8270, 8410
Dicamba	8151, 8321
Dichlone	8081, 8270
3,4-Dichloroaniline	8131
1,2-Dichlorobenzene	8021, 8121, 8260, 8270, 8410

TABLE 2-1. (Continued)

Analyte	Applicable Method(s)
1,3-Dichlorobenzene	8021, 8121, 8260, 8270, 8410
1,4-Dichlorobenzene	8021, 8121, 8260, 8270, 8410
3,3'-Dichlorobenzidine	8270,8325
3,5-Dichlorobenzoic acid	8151
2,3-Dichlorobiphenyl	8082, 8275
3,3'-Dichlorobiphenyl	8275
cis-1,4-Dichloro-2-butene	8260
trans-1,4-Dichloro-2-butene	8260
Dichlorodifluoromethane	8021, 8260
1,1-Dichloroethane	8021, 8260
1,2-Dichloroethane	8021, 8260
1,1-Dichloroethene (Vinylidene chloride)	8021, 8260
cis-1,2-Dichloroethene	8021, 8260
trans-1,2-Dichloroethene	8021, 8260
Dichlorofenthion	8141
Dichloromethane (DCM, Methylene chloride)	8021, 8260
2,6-Dichloro-4-nitroaniline	8131
2,3-Dichloronitrobenzene	8091
2,4-Dichloronitrobenzene	8091
3,5-Dichloronitrobenzene	8091
3,4-Dichloronitrobenzene	8091
2,5-Dichloronitrobenzene	8091
2,3-Dichlorophenol	8041
2,4-Dichlorophenol	8041, 8270, 8410
2,5-Dichlorophenol	8041
2,6-Dichlorophenol	8041, 8270
3,4-Dichlorophenol	8041
3,5-Dichlorophenol	8041
2,4-Dichlorophenol 3-methyl-4-nitrophenyl ether	8111
2,6-Dichlorophenyl 4-nitrophenyl ether	8111
3,5-Dichlorophenyl 4-nitrophenyl ether	8111
2,5-Dichlorophenyl 4-nitrophenyl ether	8111
2,4-Dichlorophenyl 4-nitrophenyl ether	8111
2,3-Dichlorophenyl 4-nitrophenyl ether	8111
3,4-Dichlorophenyl 4-nitrophenyl ether	8111
Dichloroprop (Dichlorprop)	8151, 8321
1,2-Dichloropropane	8021, 8260
1,3-Dichloropropane	8021, 8260
2,2-Dichloropropane	8021, 8260
1,3-Dichloro-2-propanol	8021, 8260
1,1-Dichloropropene	8021, 8260
cis-1,3-Dichloropropene	8021, 8260
trans-1,3-Dichloropropene	8021, 8260
Dichlorovos (DDVP, Dichlorvos)	8141, 8270, 8321
Dichlorprop (Dichloroprop)	8151, 8321
Dichlorvos (DDVP, Dichlorovos)	8141, 8270, 8321

Analyte	Applicable Method(s)
Dicrotophos	8141, 8270
Dicofol	8081
Dicyclohexyl phthalate	8061
Dieldrin	8081, 8270
1,2,3,4-Diepoxybutane	8260
Diesel range organics (DRO)	8015, 8440
Diethylene glycol	8430
Diethyl ether	8015, 8260
Diethyl phthalate	8061, 8270, 8410
Diethylstilbestrol	8270
Diethyl sulfate	8270
1,4-Difluorobenzene	8260
Dihexyl phthalate	8061
Dihydrosaffrole	8270
Diisobutyl phthalate	8061
Dimethoate	8141, 8270, 8321
3,3'-Dimethoxybenzidine	8270, 8325
Dimethylaminoazobenzene	8270
2,5-Dimethylbenzaldehyde	8315
7,12-Dimethylbenz(a)anthracene	8270
3,3'-Dimethylbenzidine	8270, 8325
α,α-Dimethylphenethylamine	8270
2,3-Dimethylphenol	8041
2,4-Dimethylphenol	8041, 8270
2,5-Dimethylphenol	8041
2,6-Dimethylphenol	8041
3,4-Dimethylphenol	8041
Dimethyl phthalate	8061, 8270, 8410
Dinitramine	8091
2,4-Dinitroaniline	8131
1,2-Dinitrobenzene	8091, 8270
1,3-Dinitrobenzene (1,3-DNB)	8091, 8270, 8330
1,4-Dinitrobenzene	8091, 8270
4,6-Dinitro-2-methylphenol	8270, 8410
2,4-Dinitrophenol	8041, 8270, 8410
2,5-Dinitrophenol	8041
2,4-Dinitrotoluene (2,4-DNT)	8091, 8270, 8330, 8410
2,6-Dinitrotoluene (2,6-DNT)	8091, 8270, 8330, 8410
Dinocap	8270
Dinonyl phthalate	8061
Dinoseb (2-sec-Butyl-4,6-dinitrophenol, DNBP)	8041, 8151, 8270, 8321
Di-n-octyl phthalate	8061, 8270, 8410
Dioxacarb	8318
1,4-Dioxane	8015, 8260
Dioxathion	8141, 8270
Di-n-propyl phthalate	8410

Analyte	Applicable Method(s)
Diphenylamine	8270
5,5-Diphenylhydantoin	8270
1,2-Diphenylhydrazine	8270
Disperse Blue 3	8321
Disperse Blue 14	8321
Disperse Brown 1	8321
Disperse Orange 3	8321
Disperse Orange 30	8321
Disperse Red 1	8321
Disperse Red 5	8321
Disperse Red 13	8321
Disperse Red 60	8321
Disperse Yellow 5	8321
Disulfoton	8141, 8270, 8321
Diuron	8321, 8325
1,3-DNB (1,3-Dinitrobenzene)	8091, 8270, 8330
DNBP (2-sec-Butyl-4,6-dinitrophenol, Dinoseb)	8151, 8270, 8321
2,4-DNT (2,4-Dinitrotoluene)	8091, 8270, 8275, 8330, 8410
2,6-DNT (2,6-Dinitrotoluene)	8091, 8270, 8330, 8410
EDB (1,2-Dibromoethane, Ethylene dibromide)	8011, 8021, 8260
Endosulfan I	8081, 8270
Endosulfan II	8081, 8270
Endosulfan sulfate	8081, 8270
Endrin	8081, 8270
Endrin aldehyde	8081, 8270
Endrin ketone	8081, 8270
Epichlorohydrin	8021, 8260
EPN	8141, 8270
Ethanol	8015, 8260
Ethion	8141, 8270
Ethoprop	8141
Ethyl acetate	8015, 8260
Ethylbenzene	8021, 8260
Ethyl carbamate	8270
Ethyl cyanide (Propionitrile)	8015, 8260
Ethylene dibromide (EDB, 1,2-Dibromoethane)	8011, 8021, 8260
Ethylene glycol	8015, 8430
Ethylene oxide	8015, 8260
Ethyl methacrylate	8260
Ethyl methanesulfonate	8270
Etridiazole	8081
Famphur	8141, 8270, 8321
Fenitrothion	8141
Fensulfothion	8141, 8270, 8321
Fenthion	8141, 8270
Fenuron	8321

TABLE 2-1. (Continued)

Analyte	Applicable Method(s)
Fluchloralin	8270
Fluometuron	8321
Fluoranthene	8100, 8270, 8275, 8310, 8410
Fluorene	8100, 8270, 8275, 8310, 8410
Fluorescent Brightener 61	8321
Fluorescent Brightener 236	8321
Fluorobenzene	8260
2-Fluorobiphenyl	8270
2-Fluorophenol	8270
Fonophos	8141
Formaldehyde	8315
Furaden (Carbofuran)	8270, 8318, 8321
Gasoline range organics (GRO)	8015
Halowax-1000	8081
Halowax-1001	8081
Halowax-1013	8081
Halowax-1014	8081
Halowax-1051	8081
Halowax-1099	8081
Heptachlor	8081, 8270
2,2',3,3',4,4',5-Heptachlorobiphenyl	8082, 8275
2,2',3,4,4',5,5'-Heptachlorobiphenyl	8082, 8275
2,2',3,4,4',5',6-Heptachlorobiphenyl	8082
2,2',3,4',5,5',6-Heptachlorobiphenyl	8082, 8275
Heptachlor epoxide	8081, 8270
Heptanal	8315
Hexachlorobenzene	8081, 8121, 8270, 8275, 8410
2,2',3,3,4,4'-Hexachlorobiphenyl	8275
2,2',3,4,4',5'-Hexachlorobiphenyl	8082, 8275
2,2',3,4,5,5'-Hexachlorobiphenyl	8082
2,2',3,5,5',6-Hexachlorobiphenyl	8082
2,2',4,4',5,5'-Hexachlorobiphenyl	8082
Hexachlorobutadiene	8021, 8121, 8260, 8270, 8410
α-Hexachlorocyclohexane (α-BHC)	8081, 8121, 8270
β-Hexachlorocyclohexane (β-BHC)	8081, 8121, 8270
δ-Hexachlorocyclohexane (δ-BHC)	8081, 8121, 8270
γ-Hexachlorocyclohexane (γ-BHC, Lindane)	8081, 8121, 8270
Hexachlorocyclopentadiene	8081, 8121, 8270, 8410
Hexachloroethane	8121, 8260, 8270, 8410
Hexachlorophene	8270
Hexachloropropene	8270
Hexafluoro-2-methyl-2-propanol	8015
Hexafluoro-2-propanol	8015
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	8330
Hexamethylphosphoramide (HMPA)	8141, 8270
Hexanal	8315

TABLE 2-1. (Continued)

Analyte	Applicable Method(s)
2-Hexanone	8260
Hexyl 2-ethylhexyl phthalate	8061
HMPA (Hexamethylphosphoramide)	8141, 8270
HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)	8330
1,2,3,4,6,7,8-HpCDD	8280, 8290
HpCDD, total	8280
1,2,3,4,6,7,8-HpCDF	8280, 8290
1,2,3,4,7,8,9-HpCDF	8280, 8290
HpCDF, total	8280
1,2,3,4,7,8-HxCDD	8280, 8290
1,2,3,6,7,8-HxCDD	8280, 8290
1,2,3,7,8,9-HxCDD	8280, 8290
HxCDD, total	8280
1,2,3,4,7,8-HxCDF	8280, 8290
1,2,3,6,7,8-HxCDF	8280, 8290
1,2,3,7,8,9-HxCDF	8280, 8290
2,3,4,6,7,8-HxCDF	8280, 8290
HxCDF	8280
Hydroquinone	8270
3-Hydroxycarbofuran	8318, 8321
5-Hydroxydicamba	8151
2-Hydroxypropionitrile	8260
Indeno(1,2,3-cd)pyrene	8100, 8270, 8275, 8310
Iodomethane (Methyl iodide)	8260
Isobutyl alcohol (2-Methyl-1-propanol)	8015, 8260
Isodrin	8081, 8270
Isophorone	8270, 8410
Isopropalin	8091
Isopropyl alcohol (2-Propanol)	8015, 8260
Isopropylbenzene	8021, 8260
p-Isopropyltoluene	8021, 8260
Isosafrole	8270
Isovaleraldehyde	8315
Kepone	8081, 8270
Lannate (Methomyl)	8318, 8321
Leptophos	8141, 8270
Lindane (γ-Hexachlorocyclohexane, γ-BHC)	8081, 8121, 8270
Linuron (Lorox)	8321, 8325
Lorox (Linuron)	8321, 8325
Malathion	8141, 8270
Maleic anhydride	8270
Malononitrile	8260
MCPA	8151, 8321
MCPP	8151, 8321
Merphos	8141, 8321
Mestranol	8270

Analyte	Applicable Method(s)
Mesurol (Methiocarb)	8318, 8321
Methacrylonitrile	8260
Methanol	8015, 8260
Methapyrilene	8270
Methiocarb (Mesurol)	8318, 8321
Methomyl (Lannate)	8318, 8321
Methoxychlor	8081, 8270
Methyl acrylate	8260
2-Methyl-1-propanol (Isobutyl alcohol)	8015, 8260
Methyl-t-butyl ether	8260
3-Methylcholanthrene	8100, 8270
2-Methyl-4,6-dinitrophenol	8041
4,4'-Methylenebis(2-chloroaniline)	8270
4,4'-Methylenebis(N,N-dimethylaniline)	8270
Methyl ethyl ketone (MEK, 2-Butanone)	8015, 8260
Methylene chloride (Dichloromethane, DCM)	8021, 8260
Methyl iodide (Iodomethane)	8260
Methyl isobutyl ketone (MIBK, 4-Methyl-2-pentanone)	8015, 8260
Methyl methacrylate	8260
Methyl methanesulfonate	8270
2-Methylnaphthalene	8270, 8410
Methyl parathion	8270, 8321
4-Methyl-2-pentanone (MIBK, Methyl isobutyl ketone)	8015, 8260
2-Methylphenol (o-Cresol)	8041, 8270, 8410
3-Methylphenol (m-Cresol)	8041, 8270
4-Methylphenol (p-Cresol)	8041, 8270, 8410
2-Methylpyridine (2-Picoline)	8015, 8260, 8270
Methyl-2,4,6-trinitrophenylnitramine (Tetryl)	8330
Mevinphos	8141, 8270
Mexacarbate	8270, 8321
MIBK (Methyl isobutyl ketone, 4-Methyl-2-pentanone)	8015, 8260
Mirex	8081, 8270
Monocrotophos	8141, 8270, 8321
Monuron	8321, 8325
Naled	8141, 8270, 8321
Naphthalene	8021, 8100, 8260, 8270, 8275, 8310, 8410
NB (Nitrobenzene)	8091, 8260, 8270, 8330, 8410
1,2-Naphthoquinone	8091
1,4-Naphthoquinone	8270, 8091
1-Naphthylamine	8270
2-Naphthylamine	8270
Neburon	8321
Nicotine	8270
5-Nitroacenaphthene	8270
2-Nitroaniline	8131, 8270, 8410
3-Nitroaniline	8131, 8270, 8410

TABLE 2-1. (Continued)

Analyte	Applicable Method(s)
4-Nitroaniline	8131, 8270, 8410
5-Nitro-o-anisidine	8270
Nitrobenzene (NB)	8091, 8260, 8270, 8330, 8410
4-Nitrobiphenyl	8270
Nitrofen	8081, 8270
Nitroglycerin	8332
2-Nitrophenol	8041, 8270, 8410
3-Nitrophenol	8041
4-Nitrophenol	8041, 8151, 8270, 8410
4-Nitrophenyl phenyl ether	8111
2-Nitropropane	8260
Nitroquinoline-1-oxide	8270
N-Nitrosodi-n-butylamine	8015, 8260, 8270
N-Nitrosodiethylamine	8270
N-Nitrosodimethylamine	8070, 8270, 8410
N-Nitrosodi-n-butylamine (N-Nitrosodibutylamine)	8015, 8260, 8270
N-Nitrosodiphenylamine	8070, 8270, 8410
N-Nitrosodi-n-propylamine	8070, 8270, 8410
N-Nitrosomethylethylamine	8270
N-Nitrosomorpholine	8270
N-Nitrosopiperidine	8270
N-Nitrosopyrrolidine	8270
2-Nitrotoluene (o-Nitrotoluene, 2-NT)	8091, 8330
3-Nitrotoluene (m-Nitrotoluene, 3-NT)	8091, 8330
4-Nitrotoluene (p-Nitrotoluene, 4-NT)	8091, 8330
o-Nitrotoluene (2-Nitrotoluene, 2-NT)	8091, 8330
m-Nitrotoluene (3-Nitrotoluene, 3-NT)	8091, 8330
p-Nitrotoluene (4-Nitrotoluene, 4-NT)	8091, 8330
5-Nitro-o-toluidine	8270
trans-Nonachlor	8081
2,2'3,3'4,4'5,5'6-Nonachlorobiphenyl	8082, 8275
Nonanal	8315
2-NT (2-Nitrotoluene, o-Nitrotoluene)	8091, 8330
3-NT (3-Nitrotoluene, m-Nitrotoluene)	8091, 8330
4-NT (4-Nitrotoluene, p-Nitrotoluene)	8091, 8330
OCDD	8280, 8290
OCDF	8280, 8290
2,2',3,3',4,4'5,5'-Octachlorobiphenyl	8275
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	8330
Octamethyl pyrophosphoramide	8270
Octanal	8315
Oxamyl	8321
4,4'-Oxydianiline	8270
Paraldehyde	8015, 8260
Parathion	8270
Parathion, ethyl	8141

TABLE 2-1. (Continued)

Analyte	Applicable Method(s)
Parathion, methyl	8141
PCB-1016 (Aroclor-1016)	8082, 8270
PCB-1221 (Aroclor-1221)	8082, 8270
PCB-1232 (Aroclor-1232)	8082, 8270
PCB-1242 (Aroclor-1242)	8082, 8270
PCB-1248 (Aroclor-1248)	8082, 8270
PCB-1254 (Aroclor-1254)	8082, 8270
PCB-1260 (Aroclor-1260)	8082, 8270
PCNB	8081
1,2,3,7,8-PeCDD	8280, 8290
PeCDD, total	8280
1,2,3,7,8-PeCDF	8280, 8290
2,3,4,7,8-PeCDF	8280, 8290
PeCDF, total	8280
Pendimethaline (Penoxalin)	8091
Penoxalin (Pendimethaline)	8091
Pentachlorobenzene	8121, 8270
2,2',3,4,5'-Pentachlorobiphenyl	8082
2,2',4,5,5'-Pentachlorobiphenyl	8082, 8275
2,3,3',4',6-Pentachlorobiphenyl	8082
2,3',4,4',5-Pentachlorobiphenyl	8275
Pentachloroethane	8260
Pentachloronitrobenzene	8091, 8270
Pentachlorophenol	8041, 8151, 8270, 8410
Pentafluorobenzene	8260
Pentanal (Valeraldehyde)	8315
2-Pentanone	8015, 8260
Permethrin	8081
Perthane	8081
Phenacetin	8270
Phenanthrene	8100, 8270, 8275, 8310, 8410
Phenobarbital	8270
Phenol	8041, 8270, 8410
1,4-Phenylenediamine	8270
Phorate	8141, 8270, 8321
Phosalone	8270
Phosmet	8141, 8270
Phosphamidon	8141, 8270
Phthalic anhydride	8270
Picloram	8151
2-Picoline (2-Methylpyridine)	8015, 8260, 8270
Piperonyl sulfoxide	8270
Profluralin	8091
Promecarb	8318
Pronamide	8270
Propachlor	8081, 8321

TABLE 2-1. (Continued)

Analyte	Applicable Method(s)
Propanal (Propionaldehyde)	8315, 8321
1-Propanol	8015, 8260
2-Propanol (Isopropyl alcohol)	8015, 8260
Propargyl alcohol	8260
Propenal (Acrolein)	8260, 8315
Propham	8321
ß-Propiolactone	8260
Propionaldehyde (Propanal)	8315
Propionitrile (Ethyl cyanide)	8015, 8260
Propoxur (Baygon)	8318, 8321
n-Propylamine	8260
n-Propylbenzene	8021, 8260
Propylthiouracil	8270
Prothiophos (Tokuthion)	8141
Pyrene	8100, 8270, 8275, 8310, 8410
Pyridine	8015, 8260, 8270
RDX (Hexahydro-1,3,5-trinitro-1,3,5-triazine)	8330
Resorcinol	8270
Ronnel	8141
Rotenone	8325
Safrole	8270
Sevin (Carbaryl)	8270, 8318, 8321, 8325
Siduron	8321, 8325
Simazine	8141
Silvex (2,4,5-TP)	8151, 8321
Solvent Red 3	8321
Solvent Red 23	8321
Stirophos (Tetrachlorvinphos)	8141, 8270
Strobane	8081
Strychnine	8270, 8321
Styrene	8021, 8260
Sulfallate	8270
Sulfotepp	8141
Sulprofos (Bolstar)	8141
2,4,5-T	8151, 8321
2,4,5-T, butoxyethanol ester	8321
2,4,5-T, butyl ester	8321
2,3,7,8-TCDD	8280, 8290
TCDD, total	8280
2,3,7,8-TCDF	8280, 8290
TCDF, total	8280
Tebuthiuron	8321
Temik (Aldicarb)	8318, 8321
TEPP	8141
Terbufos	8141, 8270
1,2,3,4-Tetrachlorobenzene	8121

Analyte	Applicable Method(s)
1,2,3,5-Tetrachlorobenzene	8121
1,2,4,5-Tetrachlorobenzene	8121, 8270
2,2',3,5'-Tetrachlorobiphenyl	8082, 8275
2,2',4,5'-Tetrachlorobiphenyl	8275
2,2',5,5'-Tetrachlorobiphenyl	8082, 8275
2,3',4,4'-Tetrachlorobiphenyl	8082, 8275
1,1,1,2-Tetrachloroethane	8021, 8260
1,1,2,2-Tetrachloroethane	8021, 8260
Tetrachloroethene	8021, 8260
2,3,4,5-Tetrachlorophenol	8041
2,3,4,6-Tetrachlorophenol	8041, 8270
2,3,5,6-Tetrachlorophenol	8041
2,3,4,5-Tetrachloronitrobenzene	8091
2,3,5,6-Tetrachloronitrobenzene	8091
Tetrachlorvinphos (Stirophos)	8141, 8270
Tetraethyl dithiopyrophosphate	8270
Tetraethyl pyrophosphate	8270
Tetrazene	8331
Tetryl (Methyl-2,4,6-trinitrophenylnitramine)	8330
Thiofanox	8321
Thionazin (Zinophos)	8141, 8270
Thiophenol (Benzenethiol)	8270
1,3,5-TNB (1,3,5-Trinitrobenzene)	8270, 8330
2,4,6-TNT (2,4,6-Trinitrobenzene)	8330
TOCP (Tri-o-cresylphosphate)	8141
Tokuthion (Prothiophos)	8141
m-Tolualdehyde	8315
o-Tolualdehyde	8315
p-Tolualdehyde	8315
Toluene	8021, 8260
Toluene diisocyanate	8270
o-Toluidine	8015, 8260, 8270
Toxaphene	8081, 8270
2,4,5-TP (Silvex)	8151, 8321
2,4,6-Tribromophenol	8270
2,4,6-Trichloroaniline	8131
2,4,5-Trichloroaniline	8131
1,2,3-Trichlorobenzene	8021, 8121, 8260
1,2,4-Trichlorobenzene	8021, 8121, 8260, 8270, 8275, 8410
2,2',5-Trichlorobiphenyl	8082, 8275
2,3',5-Trichlorobiphenyl	8275
2,4',5-Trichlorobiphenyl	8082, 8275
1,3,5-Trichlorobenzene	8121
1,1,1-Trichloroethane	8021, 8260
1,1,2-Trichloroethane	8021, 8260
Trichloroethene	8021, 8260

TABLE 2-1. (Continued)

Analyte	Applicable Method(s)
Trichlorofluoromethane	8021, 8260
Trichlorfon	8141, 8321
Trichloronate	8141
1,2,3-Trichloro-4-nitrobenzene	8091
1,2,4-Trichloro-5-nitrobenzene	8091
2,4,6-Trichloronitrobenzene	8091
2,3,4-Trichlorophenol	8041
2,3,5-Trichlorophenol	8041
2,3,6-Trichlorophenol	8041
2,4,5-Trichlorophenol	8041, 8270, 8410
2,4,6-Trichlorophenol	8041, 8270, 8410
2,4,6-Trichlorophenyl 4-nitrophenyl ether	8111
2,3,6-Trichlorophenyl 4-nitrophenyl ether	8111
2,3,5-Trichlorophenyl 4-nitrophenyl ether	8111
2,4,5-Trichlorophenyl 4-nitrophenyl ether	8111
3,4,5-Trichlorophenyl 4-nitrophenyl ether	8111
2,3,4-Trichlorophenyl 4-nitrophenyl ether	8111
1,2,3-Trichloropropane	8021, 8260
O,O,O-Triethyl phosphorothioate	8270
Trifluralin	8091, 8081, 8270
2,4,5-Trimethylaniline	8270
1,2,4-Trimethylbenzene	8021, 8260
1,3,5-Trimethylbenzene	8021, 8260
Trimethyl phosphate	8270
1,3,5-Trinitrobenzene (1,3,5-TNB)	8270, 8330
2,4,6-Trinitrobenzene (2,4,6-TNT)	8330
Tris-BP (Tris-(2,3-dibromopropyl) phosphate)	8270, 8321
Tri-o-cresylphosphate (TOCP)	8141
Tri-p-tolyl phosphate	8270
Tris-(2,3-dibromopropyl) phosphate (Tris-BP)	8270, 8321
Valeraldehyde (Pentanal)	8315
Vinyl acetate	8260
Vinyl chloride	8021, 8260
Vinylidene chloride (1,1-Dichloroethene)	8021, 8260
o-Xylene	8021, 8260
m-Xylene	8021, 8260
p-Xylene	8021, 8260
Zinophos (Thionazin)	8141, 8270

TABLE 2-2A
METHOD 3650 (ACID-BASE PARTITION CLEANUP) - BASE/NEUTRAL FRACTION

Benz(a)anthracene	Hexachlorobenzene
Benzo(a)pyrene	Hexachlorobutadiene
Benzo(b)fluoranthene	Hexachloroethane
Chlordane	Hexachlorocyclopentadiene
Chlorinated dibenzodioxins	Naphthalene
Chrysene	Nitrobenzene
Creosote	Phorate
Dichlorobenzene(s)	2-Picoline
Dinitrobenzene	Pyridine
2,4-Dinitrotoluene	Tetrachlorobenzene(s)
Heptachlor	Toxaphene

TABLE 2-2B
METHOD 3650 (ACID-BASE PARTITION CLEANUP) - ACID FRACTION

2-Chlorophenol	4-Nitrophenol
Cresol(s)	Pentachlorophenol
Creosote	Phenol
Dichlorophenoxyacetic acid	Tetrachlorophenol(s)
2,4-Dimethylphenol	Trichlorophenol(s)
4,6-Dinitro-o-cresol	2,4,5-TP (Silvex)

TABLE 2-3
METHOD 5041 - SORBENT CARTRIDGES FROM VOLATILE ORGANIC SAMPLING TRAIN (VOST)

Acetone	1,2-Dichloropropane
Acrylonitrile	cis-1,3-Dichloropropene
Benzene	trans-1,3-Dichloropropene
Bromodichloromethane	Ethylbenzene[a]
Bromoform[a]	Iodomethane
Bromomethane[b]	Methylene chloride
Carbon disulfide	Styrene[a]
Carbon tetrachloride	1,1,2,2-Tetrachloroethane[a]
Chlorobenzene	Tetrachloroethene
Chlorodibromomethane	Toluene
Chloroethane[b]	1,1,1-Trichloroethane
Chloroform	1,1,2-Trichloroethane
Chloromethane[b]	Trichloroethene
Dibromomethane	Trichlorofluoromethane
1,1-Dichloroethane	1,2,3-Trichloropropane[a]
1,2-Dichloroethane	Vinyl chloride[b]
1,1-Dichloroethene	Xylenes[a]
trans-1,2-Dichloroethene	

[a] Boiling point of this compound is above 120°C. Method 0030 is not appropriate for quantitative sampling of this analyte.

[b] Boiling point of this compound is below 30°C. Special precautions must be taken when sampling for this analyte by Method 0030. Refer to Sec. 1 of Method 5041 for discussion.

TABLE 2-4
METHOD 8011 (MICROEXTRACTION AND GAS CHROMATOGRAPHY)

1,2-Dibromo-3-chloropropane (DBCP)
1,2-Dibromoethane (EDB)

TABLE 2-5
METHOD 8015 (GC/FID) - NONHALOGENATED VOLATILES

Acetone	Isobutyl alcohol
Acetonitrile	Isopropyl alcohol
Acrolein	Methanol
Acrylonitrile	Methyl ethyl ketone (MEK)
Allyl alcohol	Methyl isobutyl ketone (MIBK)
1-Butanol (n-Butyl alcohol)	N-Nitroso-di-n-butylamine
t-Butyl alcohol	Paraldehyde
2-Chloroacrylonitrile	2-Pentanone
Crotonaldehyde	2-Picoline
Diethyl ether	1-Propanol
1,4-Dioxane	Propionitrile
Ethanol	Pyridine
Ethyl acetate	o-Toluidine
Ethylene glycol	Gasoline range organics (GRO)
Ethylene oxide	Diesel range organics (DRO)
Hexafluoro-2-propanol	
Hexafluoro-2-methyl-2-propanol	

TABLE 2-6
METHOD 8021 (GC, PHOTOIONIZATION AND ELECTROLYTIC CONDUCTIVITY DETECTORS) - AROMATIC AND HALOGENATED VOLATILES

Allyl chloride	cis-1,2-Dichloroethene
Benzene	trans-1,2-Dichloroethene
Benzyl chloride	1,2-Dichloropropane
Bis(2-chloroisopropyl) ether	1,3-Dichloropropane
	2,2-Dichloropropane
Bromoacetone	1,3-Dichloro-2-propanol
Bromobenzene	1,1-Dichloropropene
Bromochloromethane	cis-1,3-Dichloropropene
Bromodichloromethane	trans-1,3-Dichloropropene
Bromoform	Epichlorhydrin
Bromomethane	Ethylbenzene
n-Butylbenzene	Hexachlorobutadiene
sec-Butylbenzene	Isopropylbenzene
tert-Butylbenzene	p-Isopropyltoluene
Carbon tetrachloride	Methylene chloride
Chlorobenzene	Naphthalene
Chlorodibromomethane	n-Propylbenzene
Chloroethane	Styrene
2-Chloroethanol	1,1,1,2-Tetrachloroethane
2-Chloroethyl vinyl ether	1,1,2,2-Tetrachloroethane
Chloroform	Tetrachloroethene
Chloromethyl methyl ether	Toluene
Chloroprene	1,2,3-Trichlorobenzene
Chloromethane	1,2,4-Trichlorobenzene
2-Chlorotoluene	1,1,1-Trichloroethane
4-Chlorotoluene	1,1,2-Trichloroethane
1,2-Dibromo-3-chloropropane	Trichloroethene
1,2-Dibromoethane	Trichlorofluoromethane
Dibromomethane	1,2,3-Trichloropropane
1,2-Dichlorobenzene	1,2,4-Trimethylbenzene
1,3-Dichlorobenzene	1,3,5-Trimethylbenzene
1,4-Dichlorobenzene	Vinyl chloride
Dichlorodifluoromethane	o-Xylene
1,1-Dichloroethane	m-Xylene
1,2-Dichloroethane	p-Xylene
1,1-Dichloroethene	

TABLE 2-7
METHODS 8031 AND 8032 (GC) AND 8033 (GC WITH NITROGEN-PHOSPHORUS DETECTION)

Method 8031: Acrylonitrile
Method 8032: Acrylamide
Method 8033: Acetonitrile

TABLE 2-8
METHOD 8041 (GC) - PHENOLS

2-Chloro-5-methylphenol	2,4-Dinitrophenol
4-Chloro-2-methylphenol	2,5-Dinitrophenol
4-Chloro-3-methylphenol	Dinoseb
2-Chlorophenol	2-Methyl-4,6-dinitrophenol
3-Chlorophenol	2-Methylphenol (o-Cresol)
4-Chlorophenol	3-Methylphenol (m-Cresol)
2-Cyclohexyl-4,6-dinitro-phenol	4-Methylphenol (p-Cresol)
	2-Nitrophenol
2,3-Dichlorophenol	3-Nitrophenol
2,4-Dichlorophenol	4-Nitrophenol
2,5-Dichlorophenol	Pentachlorophenol
2,6-Dichlorophenol	Phenol
3,4-Dichlorophenol	2,3,4,5-Tetrachlorophenol
3,5-Dichlorophenol	2,3,4,6-Tetrachlorophenol
2,3-Dimethylphenol	2,3,5,6-Tetrachlorophenol
2,4-Dimethylphenol	2,3,4-Trichlorophenol
2,5-Dimethylphenol	2,3,5-Trichlorophenol
2,6-Dimethylphenol	2,3,6-Trichlorophenol
3,4-Dimethylphenol	2,4,5-Trichlorophenol
	2,4,6-Trichlorophenol

TABLE 2-9
METHOD 8061 (GC/ECD) - PHTHALATE ESTERS

Benzyl benzoate	Dicyclohexyl phthalate
Bis(2-n-butoxyethyl) phthalate	Dihexyl phthalate
Bis(2-ethoxyethyl) phthalate	Diisobutyl phthalate
Bis(2-ethylhexyl) phthalate	Di-n-butyl phthalate
Bis(2-methoxyethyl) phthalate	Diethyl phthalate
Bis(4-methyl-2-pentyl)-phthalate	Dinonyl phthalate
	Dimethyl phthalate
Butyl benzyl phthalate	Di-n-octyl phthalate
Diamyl phthalate	Hexyl 2-ethylhexyl phthalate

TABLE 2-10
METHOD 8070 (GC) - NITROSAMINES

N-Nitrosodimethylamine
N-Nitrosodiphenylamine
N-Nitrosodi-n-propylamine

TABLE 2-11
METHOD 8081 (GC) - ORGANOCHLORINE PESTICIDES AND PCBs

Alachlor	Dichlone	Hexachlorobenzene
Aldrin	Dicofol	Hexachlorocyclo-pentadiene
α-BHC	Dieldrin	Isodrin
β-BHC	Endosulfan I	Kepone
δ-BHC	Endosulfan II	Methoxychlor
γ-BHC (Lindane)	Endosulfan sulfate	Mirex
Captafol	Endrin	Nitrofen
Chlorobenzilate	Endrin aldehyde	trans-Nonachlor
α-Chlordane	Endrin ketone	PCNB
γ-Chlordane	Etridiazole	Permethrin
Chlordane (NOS)	Halowax-1000	Perthane
Chloroneb	Halowax-1001	Propachlor
Chloropropylate	Halowax-1013	Strobane
Chlorothalonil	Halowax-1014	Toxaphene
DBCP	Halowax-1051	Trifluralin
DCPA	Halowax-1099	
4,4'-DDD	Heptachlor	
4,4'-DDE	Heptachlor epoxide	
4,4'-DDT		
Diallate		

TABLE 2-12
METHOD 8082 (GC) - POLYCHLORINATED BIPHENYLS

Aroclor 1016	2,2',3,4,5'-Pentachlorobiphenyl
Aroclor 1221	2,2',4,5,5'-Pentachlorobiphenyl
Aroclor 1232	2,3,3',4',6-Pentachlorobiphenyl
Aroclor 1242	2,2',3,4,4',5'-Hexachlorobiphenyl
Aroclor 1248	2,2',3,4,5,5'-Hexachlorobiphenyl
Aroclor 1254	2,2',3,5,5',6-Hexachlorobiphenyl
Aroclor 1260	2,2',4,4',5,5'-Hexachlorobiphenyl
2-Chlorobiphenyl	2,2',3,3',4,4',5-Heptachlorobiphenyl
2,3-Dichlorobiphenyl	2,2',3,4,4',5,5'-Heptachlorobiphenyl
2,2',5-Trichlorobiphenyl	2,2',3,4,4',5',6-Heptachloro-biphenyl
2,4',5-Trichlorobiphenyl	
2,2',3,5'-Tetrachlorobiphenyl	2,2',3,4',5,5',6-Heptachlorobiphenyl
2,2',5,5'-Tetrachlorobiphenyl	2,2',3,3',4,4',5,5',6-Nonachloro-biphenyl
2,3',4,4'-Tetrachlorobiphenyl	

TABLE 2-13
METHOD 8091 (GC) - NITROAROMATICS AND CYCLIC KETONES

Benefin	2,4-Dinitrotoluene
Butralin	2,6-Dinitrotoluene
1-Chloro-2,4-dinitrobenzene	Isopropalin
1-Chloro-3,4-dinitrobenzene	1,2-Naphthoquinone
1-Chloro-2-nitrobenzene	1,4-Naphthoquinone
1-Chloro-4-nitrobenzene	Nitrobenzene
2-Chloro-6-nitrotoluene	2-Nitrotoluene
4-Chloro-2-nitrotoluene	3-Nitrotoluene
4-Chloro-3-nitrotoluene	4-Nitrotoluene
2,3-Dichloronitrobenzene	Penoxalin [Pendimethalin]
2,4-Dichloronitrobenzene	Pentachloronitrobenzene
3,5-Dichloronitrobenzene	Profluralin
3,4-Dichloronitrobenzene	2,3,4,5-Tetrachloronitrobenzene
2,5-Dichloronitrobenzene	2,3,5,6-Tetrachloronitrobenzene
Dinitramine	1,2,3-Trichloro-4-nitrobenzene
1,2-Dinitrobenzene	1,2,4-Trichloro-5-nitrobenzene
1,3-Dinitrobenzene	2,4,6-Trichloronitrobenzene
1,4-Dinitrobenzene	Trifluralin

TABLE 2-14
METHOD 8100 - POLYNUCLEAR AROMATIC HYDROCARBONS

Acenaphthene	Dibenz(a,h)anthracene
Acenaphthylene	7H-Dibenzo(c,g)carbazole
Anthracene	Dibenzo(a,e)pyrene
Benz(a)anthracene	Dibenzo(a,h)pyrene
Benzo(b)fluoranthene	Dibenzo(a,i)pyrene
Benzo(j)fluoranthene	Fluoranthene
Benzo(k)fluoranthene	Fluorene
Benzo(g,h,i)perylene	Indeno(1,2,3-cd)pyrene
Benzo(a)pyrene	3-Methylcholanthrene
Chrysene	Naphthalene
Dibenz(a,h)acridine	Phenanthrene
Dibenz(a,j)acridine	Pyrene

TABLE 2-15
METHOD 8111 (GC) - HALOETHERS

Bis(2-chloroethoxy)methane	2,3-Dichlorophenyl 4-nitrophenyl ether
Bis(2-chloroethyl) ether	3,4-Dichlorophenyl 4-nitrophenyl ether
Bis(2-chloroisopropyl) ether	4-Nitrophenyl phenyl ether
4-Bromophenyl phenyl ether	2,4,6-Trichlorophenyl 4-nitrophenyl ether
4-Chlorophenyl phenyl ether	2,3,6-Trichlorophenyl 4-nitrophenyl ether
2-Chlorophenyl 4-nitrophenyl ether	2,3,5-Trichlorophenyl 4-nitrophenyl ether
3-Chlorophenyl 4-nitrophenyl ether	2,4,5-Trichlorophenyl 4-nitrophenyl ether
4-Chlorophenyl 4-nitrophenyl ether	3,4,5-Trichlorophenyl 4-nitrophenyl ether
2,4-Dibromophenyl 4-nitrophenyl ether	2,3,4-Trichlorophenyl 4-nitrophenyl ether
2,4-Dichlorophenyl 3-methyl-4-nitrophenyl ether	
2,6-Dichlorophenyl 4-nitrophenyl ether	
3,5-Dichlorophenyl 4-nitrophenyl ether	
2,5-Dichlorophenyl 4-nitrophenyl ether	
2,4-Dichlorophenyl 4-nitrophenyl ether	

TABLE 2-16
METHOD 8121 (GC) - CHLORINATED HYDROCARBONS

Benzal chloride	δ-Hexachlorocyclohexane [δ-BHC]
Benzotrichloride	γ-Hexachlorocyclohexane [γ-BHC]
Benzyl chloride	Hexachlorocyclopentadiene
2-Chloronaphthalene	Hexachloroethane
1,2-Dichlorobenzene	Pentachlorobenzene
1,3-Dichlorobenzene	1,2,3,4-Tetrachlorobenzene
1,4-Dichlorobenzene	1,2,3,5-Tetrachlorobenzene
Hexachlorobenzene	1,2,4,5-Tetrachlorobenzene
Hexachlorobutadiene	1,2,3-Trichlorobenzene
α-Hexachlorocyclohexane [α-BHC]	1,2,4-Trichlorobenzene
β-Hexachlorocyclohexane [β-BHC]	1,3,5-Trichlorobenzene

TABLE 2-17
METHOD 8131 (GC) - ANILINE AND SELECTED DERIVATIVES

Aniline	2,6-Dibromo-4-nitroaniline
4-Bromoaniline	3,4-Dichloroaniline
2-Bromo-6-chloro-4-nitroanilne	2,6-Dichloro-4-nitroaniline
2-Bromo-4,6-dintroaniline	2,4-Dinitroaniline
2-Chloroaniline	2-Nitroaniline
3-Chloroaniline	3-Nitroaniline
4-Chloroaniline	4-Nitroaniline
2-Chloro-4,6-dinitroaniline	2,4,6-Trichloroaniline
2-Chloro-4-nitroaniline	2,4,5-Trichloroaniline
4-Chloro-2-nitroaniline	

TABLE 2-18
METHOD 8141 (GC) - ORGANOPHOSPHORUS COMPOUNDS

Aspon	Fenthion
Atrazine	Fonophos
Azinphos-ethyl	Hexamethylphosphoramide (HMPA)
Azinphos-methyl	Leptophos
Bolstar (Sulprofos)	Malathion
Carbophenothion	Merphos
Chlorofenvinphos	Mevinphos
Chlorpyrifos	Monocrotophos
Chlorpyrifos methyl	Naled
Coumaphos	Parathion, ethyl
Crotoxyphos	Parathion, methyl
Demeton-O, and -S	Phorate
Diazinon	Phosmet
Dichlorofenthion	Phosphamidon
Dichlorvos (DDVP)	Ronnel
Dicrotophos	Simazine
Dimethoate	Stirophos (Tetrachlorvinphos)
Dioxathion	Sulfotepp
Disulfoton	TEPP
EPN	Terbufos
Ethion	Thionazin (Zinophos)
Ethoprop	Tokuthion (Prothiophos)
Famphur	Trichlorfon
Fenitrothion	Trichloronate
Fensulfothion	Tri-o-cresylphosphate (TOCP)

TABLE 2-19
METHOD 8151 (GC USING METHYLATION OR PENTAFLUOROBENZYLATION DERIVATIZATON) - CHLORINATED HERBICIDES

Acifluorfen	Dicamba	MCPP
Bentazon	3,5-Dichlorobenzoic acid	4-Nitrophenol
Chloramben	Dichloroprop	Pentachlorophenol
2,4-D	Dinoseb	Picloram
Dalapon	5-Hydroxydicamba	2,4,5-TP (Silvex)
2,4-DB	MCPA	2,4,5-T
DCPA diacid		

TABLE 2-20
METHOD 8260 (GC/MS)- VOLATILE ORGANIC COMPOUNDS

Acetone
Acetonitrile
Acrolein (Propenal)
Acrylonitrile
Allyl alcohol
Allyl chloride
Benzene
Benzyl chloride
Bis(2-chloroethyl)-sulfide
Bromoacetone
Bromobenzene
Bromochloromethane
Bromodichloromethane
4-Bromofluorobenzene
Bromoform
Bromomethane
n-Butanol
2-Butanone (MEK)
t-Butyl alcohol
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Carbon disulfide
Carbon tetrachloride
Chloral hydrate
Chloroacetonitrile
Chlorobenzene
1-Chlorobutane
Chlorodibromomethane
Chloroethane
2-Chloroethanol
2-Chloroethyl vinyl ether
Chloroform
1-Chlorohexane
Chloromethane
Chloroprene
3-Chloropropionitrile
2-Chlorotoluene
4-Chlorotoluene
Crotonaldehyde
1,2-Dibromo-3-chloropropane
1,2-Dibromoethane
Dibromofluoromethane
Dibromomethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
cis-1,4-Dichloro-2-butene
trans-1,4-Dichloro-2-butene
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
cis-1,2-Dichloroethene
trans-1,2-Dichloro-ethene
1,2-Dichloropropane
1,3-Dichloropropane
2,2-Dichloropropane
1,3-Dichloro-2-propanol
1,1-Dichloropropene
cis-1,3-Dichloropropene
trans-1,3-Dichloro-propene
1,2,3,4-Diepoxybutane
Diethyl ether
1,4-Difluorobenzene
1,4-Dioxane
Epichlorohydrin
Ethanol
Ethyl acetate
Ethylbenzene
Ethylene oxide
Ethyl methacrylate
Fluorobenzene
Hexachlorobutadiene
Hexachloroethane
2-Hexanone
2-Hydroxypropionitrile
Iodomethane
Isobutyl alcohol
Isopropylbenzene
p-Isopropyltoluene
Malononitrile
Methacrylonitrile
Methanol
Methyl-t-butyl ether
Methylene chloride
Methyl acrylate
Methyl methacrylate
4-Methyl-2-pentanone (MIBK)
Naphthalene
Nitrobenzene
2-Nitropropane
N-Nitroso-di-n-butylamine
Paraldehyde
Pentachloroethane
Pentafluorobenzene
2-Pentanone
2-Picoline
1-Propanol
2-Propanol
Propargyl alcohol
ß-Propiolactone
Propionitrile (Ethyl cyanide)
n-Propylamine
n-Propylbenzene
Pyridine
Styrene
1,1,1,2-Tetrachloro-ethane
1,1,2,2-Tetrachloro-ethane
Tetrachloroethene
Toluene
o-Toluidine
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichlorofluoromethane
1,2,3-Trichloropropane
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
Vinyl acetate
Vinyl chloride
o-Xylene
m-Xylene
p-Xylene

TABLE 2-21
METHOD 8270 (GC/MS) - SEMIVOLATILE ORGANIC COMPOUNDS

Acenaphthene
Acenaphthylene
Acetophenone
2-Acetylaminofluorene
1-Acetyl-2-thiourea
Aldrin
2-Aminoanthraquinone
Aminoazobenzene
4-Aminobiphenyl
3-Amino-9-ethyl-carbazole
Anilazine
Aniline
o-Anisidine
Anthracene
Aramite
Aroclor-1016
Aroclor-1221
Aroclor-1232
Aroclor-1242
Aroclor-1248
Aroclor-1254
Aroclor-1260
Azinphos-methyl
Barban
Benz(a)anthracene
Benzidine
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzoic acid
Benzo(g,h,i)perylene
Benzo(a)pyrene
p-Benzoquinone
Benzyl alcohol
α-BHC
β-BHC
δ-BHC
γ-BHC (Lindane)
Bis(2-chloroethoxy)-methane
Bis(2-chloroethyl) ether
Bis(2-chloroisopropyl) ether
Bis(2-ethylhexyl) phthalate
4-Bromophenyl phenyl ether
Bromoxynil
Butyl benzyl phthalate
Captafol
Captan
Carbaryl
Carbofuran
Carbophenothion
Chlordane (NOS)
Chlorfenvinphos
4-Chloroaniline
Chlorobenzilate
5-Chloro-2-methyl-aniline
4-Chloro-3-methylphenol
3-(Chloromethyl)-pyridine hydro-chloride
1-Chloronaphthalene
2-Chloronaphthalene
2-Chlorophenol
4-Chloro-1,2-phenylene-diamine
4-Chloro-1,3-phenylene-diamine
4-Chlorophenyl phenyl ether
Chrysene
Coumaphos
p-Cresidine
Crotoxyphos
2-Cyclohexyl-4,6-dinitrophenol
4,4'-DDD
4,4'-DDE
4,4'-DDT
Demeton-O
Demeton-S
Diallate (cis or trans)
2,4-Diaminotoluene
Dibenz(a,j)acridine
Dibenz(a,h)anthracene
Dibenzofuran
Dibenzo(a,e)pyrene
1,2-Dibromo-3-chloropropane
Di-n-butyl phthalate
Dichlone
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
3,3'-Dichlorobenzidine
2,4-Dichlorophenol
2,6-Dichlorophenol
Dichlorovos
Dicrotophos
Dieldrin
Diethyl phthalate
Diethylstilbestrol
Diethyl sulfate
Dihydrosaffrole
Dimethoate
3,3'-Dimethoxybenzidine
Dimethylaminoazobenzene
7,12-Dimethylbenz(a)-anthracene
3,3'-Dimethylbenzidine
α,α-Dimethylphenethyl-amine
2,4-Dimethylphenol
Dimethyl phthalate
1,2-Dinitrobenzene
1,3-Dinitrobenzene
1,4-Dinitrobenzene
4,6-Dinitro-2-methyl-phenol
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Dinocap
Dinoseb
Dioxathion
Diphenylamine
5,5-Diphenylhydantoin
1,2-Diphenylhydrazine
Di-n-octyl phthalate
Disulfoton
Endosulfan I
Endosulfan II
Endosulfan sulfate
Endrin
Endrin aldehyde
Endrin ketone
EPN
Ethion
Ethyl carbamate
Ethyl methanesulfonate

Famphur
Fensulfothion
Fenthion
Fluchloralin
Fluoranthene
Fluorene
2-Fluorobiphenyl
2-Fluorophenol
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclo-
pentadiene
Hexachloroethane
Hexachlorophene
Hexachloropropene
Hexamethylphosphoramide
Hydroquinone
Indeno(1,2,3-cd)pyrene
Isodrin
Isophorone
Isosafrole
Kepone
Leptophos
Malathion
Maleic anhydride
Mestranol
Methapyrilene
Methoxychlor
3-Methylcholanthrene
4,4'-Methylenebis-
(2-chloroaniline)
4,4'-Methylenebis-
(N,N-dimethylaniline)
Methyl methanesulfonate
2-Methylnaphthalene
Methyl parathion
2-Methylphenol
3-Methylphenol
4-Methylphenol
Mevinphos
Mexacarbate
Mirex
Monocrotophos
Naled
Naphthalene
1,4-Naphthoquinone
1-Naphthylamine
2-Naphthylamine
Nicotine
5-Nitroacenaphthene
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline
5-Nitro-o-anisidine
Nitrobenzene
4-Nitrobiphenyl
Nitrofen
2-Nitrophenol
4-Nitrophenol
Nitroquinoline-1-oxide
N-Nitrosodi-n-
butylamine
N-Nitrosodiethylamine
N-Nitrosodimethylamine
N-Nitrosodiphenylamine
N-Nitrosodi-n-propyl-
amine
N-Nitrosomethylethyl-
amine
N-Nitrosomorpholine
N-Nitrosopiperidine
N-Nitrosopyrrolidine
5-Nitro-o-toluidine
Octamethyl pyrophos-
phoramide
4,4'-Oxydianiline
Parathion
Pentachlorobenzene
Pentachloronitrobenzene
Pentachlorophenol
Phenacetin
Phenanthrene
Phenobarbital
Phenol
1,4-Phenylenediamine
Phorate
Phosalone
Phosmet
Phosphamidion
Phthalic anhydride
2-Picoline
Piperonyl sulfoxide
Pronamide
Propylthiouracil
Pyrene
Pyridine
Resorcinol
Safrole
Strychnine
Sulfallate
Terbufos
1,2,4,5-Tetrachloro
benzene
2,3,4,6-Tetrachloro-
phenol
Tetrachlorvinphos
Tetraethyl dithio-
pyrophosphate
Tetraethyl
pyrophosphate
Thionazine
Thiophenol
(Benzenethiol)
Toluene diisocyanate
o-Toluidine
Toxaphene
2,4,6-Tribromophenol
1,2,4-Trichlorobenzene
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
O,O,O-Triethyl
phosphorothioate
Trifluralin
2,4,5-Trimethylaniline
Trimethyl phosphate
1,3,5-Trinitrobenzene
Tris(2,3-dibromopropyl)
phosphate
Tri-p-tolyl phosphate

TABLE 2-22
METHOD 8275 (TE/GC/MS) - SEMIVOLATILE ORGANIC COMPOUNDS

Acenaphthene	Pyrene	2,3',4,4',5-Penta-chlorobiphenyl
Acenaphthylene	1,2,4-Trichlorobenzene	2,2',3,4,4',5'-Hexachlorobiphenyl
Anthracene	2-Chlorobiphenyl	2,2',3,3',4,4'-Hexachlorobiphenyl
Benz(a)anthracene	3,3'-Dichlorobiphenyl	2,2',3,4',5,5',6-Heptachlorobiphenyl
Benzo(a)pyrene	2,2',5-Trichloro-biphenyl	2,2',3,4,4',5,5'-Heptachlorobiphenyl
Benzo(b)fluoranthene	2,3',5-Trichloro-biphenyl	2,2',3,3',4,4',5-Heptachlorobiphenyl
Benzo(g,h,i)perylene	2,4',5-Trichloro-biphenyl	2,2',3,3',4,4',5,5'-Octachlorobiphenyl
Benzo(k)fluoranthene	2,2',5,5'-Tetrachloro-biphenyl	2,2',3,3'4,4',5,5',6-Nonachlorobiphenyl
4-Bromophenyl phenyl ether	2,2'4,5'-Tetrachloro-biphenyl	2,2',3,3'4,4',5,5',6,6'-Decachlorobiphenyl
1-Chloronaphthalene	2,2'3,5'-Tetrachloro-biphenyl	
Chrysene	2,3',4,4'-Tetrachloro-biphenyl	
Dibenzofuran	2,2',4,5,5'-Penta-chlorobiphenyl	
Dibenz(a,h)anthracene		
Dibenzothiophene		
Fluoranthene		
Fluorene		
Hexachlorobenzene		
Indeno(1,2,3-cd)pyrene		
Naphthalene		
Phenanthrene		

TABLE 2-23
METHODS 8280 (HRGC/LRMS) AND 8290 (HRGC/HRMS) -
POLYCHLORINATED DIBENZO-*p*-DIOXINS (PCDDs)
AND POLYCHLORINATED DIBENZOFURANS (PCDFs)

2,3,7,8-TCDD	HpCDD, total*	1,2,3,7,8,9-HxCDF
TCDD, total*	OCDD	2,3,4,6,7,8-HxCDF
1,2,3,7,8-PeCDD	2,3,7,8-TCDF	HxCDF, total*
PeCDD, total*	TCDF, total*	1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8-HxCDD	1,2,3,7,8-PeCDF	1,2,3,4,7,8,9-HpCDF
1,2,3,6,7,8-HxCDD	2,3,4,7,8-PeCDF	HpCDF, total*
1,2,3,7,8,9-HxCDD	PeCDF, total*	OCDF
HxCDD, total*	1,2,3,4,7,8-HxCDF	
1,2,3,4,6,7,8-HpCDD	1,2,3,6,7,8-HxCDF	

* Analyte of only Method 8280.

TABLE 2-24
METHOD 8310 (HPLC) - POLYNUCLEAR AROMATIC HYDROCARBONS

Acenaphthene	Chrysene
Acenaphthylene	Dibenzo(a,h)anthracene
Anthracene	Fluoranthene
Benzo(a)anthracene	Fluorene
Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene
Benzo(b)fluoranthene	Naphthalene
Benzo(g,h,i)perylene	Phenanthrene
Benzo(k)fluoranthene	Pyrene

TABLE 2-25
METHOD 8315 - CARBONYL COMPOUNDS

Acetaldehyde	Hexanal (Hexaldehyde)
Acetone	Isovaleraldehyde
Acrolein	Nonanal
Benzaldehyde	Octanal
Butanal (Butyraldehyde)	Pentanal (Valeraldehyde)
Crotonaldehyde	Propanal
Cyclohexanone	(Propionaldehyde)
Decanal	m-Tolualdehyde
2,5-Dimethylbenzaldehyde	o-Tolualdehyde
Formaldehyde	p-Tolualdehyde
Heptanal	

TABLE 2-26
METHOD 8316 (HPLC)

Acrylamide
Acrylonitrile
Acrolein

TABLE 2-27
METHOD 8318 (HPLC) - N-METHYLCARBAMATES

Aldicarb (Temik)
Aldicarb sulfone
Carbaryl (Sevin)
Carbofuran (Furadan)
Dioxacarb
3-Hydroxycarbofuran
Methiocarb (Mesurol)
Methomyl (Lannate)
Promecarb
Propoxur (Baygon)

TABLE 2-28. METHOD 8321 (HPLC/TS/MS) - NONVOLATILE ORGANIC COMPOUNDS

Azo Dyes
Disperse Red 1
Disperse Red 5
Disperse Red 13
Disperse Yellow 5
Disperse Orange 3
Disperse Orange 30
Disperse Brown 1
Solvent Red 3
Solvent Red 23

Chlorinated Phenoxyacid Compounds
2,4-D
2,4-D, butoxyethanol ester
2,4-D, ethylhexyl ester
2,4-DB
Dalapon
Dicamba
Dichlorprop
Dinoseb
MCPA
MCPP
Silvex (2,4,5-TP)
2,4,5-T
2,4,5-T, butyl ester
2,4,5-T, butoxyethanol ester

Alkaloids
Strychnine
Caffeine

Organophosphorus Compounds
Asulam
Fensulfothion
Dichlorvos
Dimethoate
Disulfoton
Merphos
Methomyl
Methyl parathion
Monocrotophos
Famphur
Naled
Phorate
Trichlorfon
Thiofanox
Tris(2,3-dibromopropyl) phosphate (Tris-BP)

Anthraquinone Dyes

Disperse Blue 3
Disperse Blue 14
Disperse Red 60
Coumarin Dyes

Fluorescent Brighteners

Fluorescent Brightener 61
Fluorescent Brightener 236

Carbamates

Aldicarb
Aldicarb sulfone
Aldicarb sulfoxide
Aminocarb
Barban
Benomyl
Bromacil
Bendiocarb
Carbaryl
Carbendazim
Carbofuran
3-Hydroxycarbofuran
Chloroxuron
Chloropropham
Diuron
Fenuron
Fluometuron
Linuron
Methiocarb
Methomyl
Mexacarbate
Monuron
Neburon
Oxamyl
Propachlor
Propham
Propoxur
Siduron
Tebuthiuron

TABLE 2-29
METHOD 8325 (HPLC/PB/MS) - NONVOLATILE ORGANIC COMPOUNDS

Benzidine	3,3'-Dimethylbenzidine
Benzoylprop ethyl	Diuron
Carbaryl	Linuron (Lorox)
o-Chlorophenyl thiourea	Monuron
3,3'-Dichlorobenzidine	Rotenone
3,3'-Dimethoxybenzidine	Siduron

TABLE 2-30
METHOD 8330 (HPLC) - NITROAROMATICS AND NITRAMINES

4-Amino-2,6-dinitrotoluene (4-Am-DNT)	Nitrobenzene (NB)
2-Amino-4,6-dinitrotoluene (2-Am-DNT)	2-Nitrotoluene (2-NT)
1,3-Dinitrobenzene (1,3-DNB)	3-Nitrotoluene (3-NT)
2,4-Dinitrotoluene (2,4-DNT)	4-Nitrotoluene (4-NT)
2,6-Dinitrotoluene (2,6-DNT)	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	1,3,5-Trinitrobenzene (1,3,5-TNB)
Methyl-2,4,6-trinitrophenyl-nitramine (Tetryl)	2,4,6-Trinitrotoluene (2,4,6-TNT)

TABLE 2-31
METHOD 8331 (REVERSE PHASE HPLC)

Tetrazene

TABLE 2-32
METHOD 8332 (HPLC)

Nitroglycerine

TABLE 2-33
METHOD 8410 - SEMIVOLATILE ORGANIC COMPOUNDS

Acenaphthene	2,6-Dinitrotoluene
Acenaphthylene	Di-n-octyl phthalate
Anthracene	Di-n-propyl phthalate
Benzo(a)anthracene	Fluoranthene
Benzo(a)pyrene	Fluorene
Benzoic acid	Hexachlorobenzene
Bis(2-chloroethoxy)methane	1,3-Hexachlorobutadiene
Bis(2-chloroethyl) ether	Hexachlorocyclopentadiene
Bis(2-chloroisopropyl) ether	Hexachloroethane
Bis(2-ethylhexyl) phthalate	Isophorone
4-Bromophenyl phenyl ether	2-Methylnaphthalene
Butyl benzyl phthalate	2-Methylphenol
4-Chloroaniline	4-Methylphenol
4-Chloro-3-methylphenol	Naphthalene
2-Chloronaphthalene	2-Nitroaniline
2-Chlorophenol	3-Nitroaniline
4-Chlorophenol	4-Nitroaniline
4-Chlorophenyl phenyl ether	Nitrobenzene
Chrysene	2-Nitrophenol
Dibenzofuran	4-Nitrophenol
Di-n-butyl phthalate	N-Nitrosodimethylamine
1,2-Dichlorobenzene	N-Nitrosodiphenylamine
1,3-Dichlorobenzene	N-Nitroso-di-n-propylamine
1,4-Dichlorobenzene	Pentachlorophenol
2,4-Dichlorophenol	Phenanthrene
Diethyl phthalate	Phenol
Dimethyl phthalate	Pyrene
4,6-Dinitro-2-methylphenol	1,2,4-Trichlorobenzene
2,4-Dinitrophenol	2,4,5-Trichlorophenol
2,4-Dinitrotoluene	2,4,6-Trichlorophenol

TABLE 2-34
METHOD 8430 (GC/FT-IR) - BIS(2-CHLOROETHYL) ETHER
AND ITS HYDROLYSIS PRODUCTS

Bis(2-chloroethyl) ether
2-Chloroethanol
2-(2-Chloroethoxy)ethanol
Diethylene glycol
Ethylene glycol

TABLE 2-35
ANALYSIS METHODS FOR INORGANIC ANALYTES

Compound	Applicable Method(s)
Aluminum	6010, 6020, 7020
Antimony	6010, 6020, 7040, 7041, 7062
Arsenic	6010, 6020, 7060, 7061, 7062, 7063
Barium	6010, 6020, 7080, 7081
Beryllium	6010, 6020, 7090, 7091
Bromide	9056, 9211
Cadmium	6010, 6020, 7130, 7131
Calcium	6010, 7140
Chloride	9056, 9057, 9212, 9250, 9251, 9253
Chromium	6010, 6020, 7190, 7191
Chromium, hexavalent	7195, 7196, 7197, 7198, 7199
Cobalt	6010, 6020, 7200, 7201
Copper	6010, 6020, 7210, 7211
Cyanide	9010, 9012, 9013, 9213
Fluoride	9056, 9214
Iron	6010, 7380, 7381
Lead	6010, 6020, 7420, 7421
Lithium	6010, 7430
Magnesium	6010, 7450
Manganese	6010, 6020, 7460, 7461
Mercury	7470, 7471, 7472
Molybdenum	6010, 7480, 7481
Nickel	6010, 6020, 7520, 7521
Nitrate	9056, 9210
Nitrite	9056
Osmium	7550
Phosphate	9056
Phosphorus	6010
Phosphorus, white	7580
Potassium	6010, 7610
Selenium	6010, 7740, 7741, 7742
Silver	6010, 6020, 7760, 7761
Sodium	6010, 7770
Strontium	6010, 7780
Sulfate	9035, 9036, 9038, 9056
Sulfide	9030, 9031, 9215
Thallium	6010, 6020, 7840, 7841
Tin	7870
Vanadium	6010, 7910, 7911
Zinc	6010, 6020, 7950, 7951

TABLE 2-36
CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES
FOR AQUEOUS MATRICES[A]

Name	Container[1]	Preservation	Maximum holding time
Inorganic Tests:			
Chloride	P, G	None required	28 days
Cyanide, total and amenable to chlorination	P, G	Cool to 4°C; if oxidizing agents present add 5 mL 0.1N $NaAsO_2$ per L or 0.06 g of ascorbic acid per L; adjust pH>12 with 50% NaOH. See Method 9010 for other interferences.	14 days
Hydrogen ion (pH)	P, G	None required	24 hours
Nitrate	P, G	Cool to 4°C	48 hours
Sulfate	P, G	Cool to 4°C	28 days
Sulfide	P, G	Cool to 4°C, add zinc acetate	7 days
Metals:			
Chromium VI	P, G	Cool to 4°C	24 hours
Mercury	P, G	HNO_3 to pH<2	28 days
Metals, except chromium VI and mercury	P, G	HNO_3 to pH<2	6 months
Organic Tests:			
Acrolein and acrylonitrile	G, PTFE-lined septum	Cool to 4°C, 0.008% $Na_2S_2O_3$[3], Adjust pH to 4-5	14 days
Benzidines	G, PTFE-lined cap	Cool to 4°C, 0.008% Na_2S_2O3[3]	7 days until extraction, 40 days after extraction
Chlorinated hydrocarbons	G, PTFE-lined cap	Cool to 4°C, 0.008% $Na_2S_2O_3$[3]	7 days until extraction, 40 days after extraction
Dioxins and Furans	G, PTFE-lined cap	Cool to 4°C, 0.008% $Na_2S_2O_3$[3]	30 days until extraction, 45 days after extraction
Haloethers	G, PTFE-lined cap	Cool to 4°C, 0.008% $Na_2S_2O_3$[3]	7 days until extraction, 40 days after extraction
Nitroaromatics and cyclic ketones	G, PTFE-lined cap	Cool to 4°C, 0.008% $Na_2S_2O_3$[3], store in dark	7 days until extraction, 40 days after extraction
Nitrosamines	G, PTFE-lined cap	Cool to 4°C, 0.008% $Na_2S_2O_3$[3], store in dark	7 days until extraction, 40 days after extraction

(continued on next page)

TABLE 2-36 (cont.)

Name	Container[1]	Preservation	Maximum holding time
Oil and grease	G	Cool to 4°C, add 5 mL diluted HCl	28 days
Organic carbon, total (TOC)	P, G	Cool to 4°C, store in dark[2]	28 days
Organochlorine pesticides	G, PTFE-lined cap	Cool to 4°C	7 days until extraction, 40 days after extraction
Organophosphorus pesticides	G, PTFE-lined cap	Cool to 4°C[4]	7 days until extraction, 40 days after extraction
PCBs	G, PTFE-lined cap	Cool to 4°C	7 days until extraction, 40 days after extraction
Phenols	G, PTFE-lined cap	Cool to 4°C, 0.008% Na_2S_2O3[3]	7 days until extraction, 40 days after extraction
Phthalate esters	G, PTFE-lined cap	Cool to 4°C	7 days until extraction, 40 days after extraction
Polynuclear aromatic hydrocarbons	G, PTFE-lined cap	Cool to 4°C, 0.008% $Na_2S_2O_3$[3], store in dark	7 days until extraction, 40 days after extraction
Purgeable aromatic hydrocarbons	G, PTFE-lined septum	Cool to 4°C, 0.008% $Na_2S_2O_3$[2,3]	14 days
Purgeable Halocarbons	G, PTFE-lined septum	Cool to 4°C, 0.008% $Na_2S_2O_3$[3]	14 days
Total organic halides (TOX)	G, PTFE-lined cap	Cool to 4°C, Adjust to pH<2 with H_2SO_4	28 days
Radiological Tests:			
Alpha, beta and radium	P, G	HNO_3 to pH<2	6 months

[A] Table originally excerpted, in part, from Table II, 49 **FR** 28, October 26, 1984, and revised as appropriate for SW-846. See Chapter Three, Chapter Four, or Section 6.0 of the individual methods for more information.

[1] Polyethylene (P) or Glass (G)

[2] Adjust to pH<2 with H_2SO_4, HCl or solid $NaHSO_4$. Free chlorine must be removed prior to adjustment.

[3] Free chlorine must be removed by the appropriate addition of $Na_2S_2O_3$.

[4] Adjust samples to pH 5-8 using NaOH or H_2SO_4.

TABLE 2-37.
PREPARATION METHODS FOR ORGANIC ANALYTES

(Note: Footnote text is located on the last page of the table.)

	Matrix			
Analyte Type	Aqueous[1]	Solids	Sludges and Emulsions[1,2]	Organic Liquids, Tars, Oils
Acid Extractable	3510 3520 (pH ≤ 2)	3540 3541 3545 3550	3520 (pH ≤ 2)	3650 3580[3]
Acrolein, Acrylonitrile, and Acetonitrile	5031	5031	5031	3585
Acrylamide	8032[4]			
Aniline and Selected Derivatives	3510 3520 (pH >11) 5031[11]	3540 3541 3545 3550	3520 (pH >11)	3580[3]
Aromatic Volatiles	5021 5030 5032	5021 5032 5035	5030 5032	3585
Base/Neutral Extractable	3510 3520 (pH >11)	3540 3541 3545 3550	3520 (pH >11)	3650 3580[3]
Carbamates	8318[5] 8321	8318[5] 8321	8318[5]	8318[5]
Chlorinated Herbicides	8151[6] (pH ≤ 2) 8321	8151[6] 8321	8151[6] (pH ≤ 2)	3580[3]
Chlorinated Hydrocarbons	3510 3520 (pH as received)	3540 3541 3550	3520 (pH as recieved)	3580[3]
Dyes	3510 3520	3540 3541 3545 3550		
Explosives	8330[7] 8331[8]	8330[7] 8331[8]		
Formaldehyde	8315[9]	8315[9]		

TABLE 2-37
PREPARATION METHODS FOR ORGANIC ANALYTES
(continued)

	Matrix			
Analyte Type	Aqueous[1]	Solids	Sludges and Emulsions[1,2]	Organic Liquids, Tars, Oils
Haloethers	3510 3520	3540 3541 3545 3550		
Halogenated Volatiles	5021 5030 5032	5021 5032 5035	5030	3585
Nitroaromatic and Cyclic Ketones	3510 3520 (pH 5-9)	3540 3541 3545 3550	3520 (pH 5-9)	3580[3]
Nitrosamines	3510 3520	3540 3541 3545 3550		
Non-halogenated Volatiles	5021 5031 5032	5021 5031 5032	5021 5031 5032	5032 3585
Organochlorine Pesticides	3510 3520 3535 (pH 5-9)	3540 3541 3545 3550	3520 (pH 5-9)	3580[3]
Organophosphorus Pesticides	3510 3520 (pH 5-8)	3540 3541 3545	3520 (pH 5-8)	3580[3]
Phenols	3510 3520 (pH $\leq$ 2)	3540 3541 3545 3550	3520 (pH $\leq$ 2)	3650 3580[3]
Phthalate Esters	3510 3520 3535 (pH 5-7)	3540 3541 3545 3550	3520 (pH 5- 7)	3580[3]
Polychlorinated Biphenyls	3510 3520 3535 (pH 5-9)	3540 3541 3545	3520 (pH 5-9)	3580[3]
PCDDs and PCDFs	8280[10] 8290[10]	8280[10] 8290[10]	8280[10] 8290[10]	8280[10] 8290[10]

TABLE 2-37
PREPARATION METHODS FOR ORGANIC ANALYTES
(continued)

	Matrix			
Analyte Type	Aqueous[1]	Solids	Sludges and Emulsions[1,2]	Organic Liquids, Tars, Oils
Polynuclear Aromatic Hydrocarbons	3510 3520 (pH as received)	3540 3541 3545 3550 3561	3520 (pH as received)	3580[3]
Volatile Organics	5021 5030 5031 5032	5021 5031 5032 5035	5021 5030 5031 5032	3585

Footnotes for Table 2-37

1 The pH at which extraction should be performed is shown in parentheses.
2 If attempts to break an emulsion are unsuccessful, these methods may be used.
3 Method 3580 is only appropriate if the sample is soluble in the specified solvent.
4 Method 8032 contains the extraction, cleanup, and determinative procedures for this analyte.
5 Method 8318 contains the extraction, cleanup, and determinative procedures for these analytes.
6 Method 8151 contains the extraction, cleanup, and determinative procedures for these analytes.
7 Method 8330 contains the extraction, cleanup, and determinative procedures for these analytes.
8 Method 8331 is for Tetrazene only, and contains the extraction, cleanup, and determinative procedures for this analyte.
9 Method 8315 contains the extraction, cleanup, and determinative procedures for this analyte.
10 Methods 8280 and 8290 contain the extraction, cleanup, and determinative procedures for these analytes.
11 Method 5031 may be used when only aniline is to be determined.

TABLE 2-38. CLEANUP METHODS FOR ORGANIC ANALYTE EXTRACTS

Analyte Type	Method
Acid Extractable	3650, 3640
Base/Neutral Extractable	3650, 3640
Carbamates	8318[1]
Chlorinated Herbicides	8151[2]
Chlorinated Hydrocarbons	3620 3640
Haloethers	3620 3640
Nitroaromatics & Cyclic Ketones	3620 3640
Nitrosamines	3610, 3620, 3640
Organochlorine Pesticides	3620 3630 3640 3660
Organophosphorus Pesticides	3620
Phenols	3630 3640 3650 8041[3]
Phthalate Esters	3610 3611 3620 3640
Polychlorinated Biphenyls	3620 3630 3640 3660 3665
Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzofurans	8280[4] 8290[4]
Polynuclear Aromatic Hydrocarbons	3610 3611 3630 3640 3650

1 Method 8318 contains the extraction, cleanup, and determinative procedures for these analytes.
2 Method 8151 contains the extraction, cleanup, and determinative procedures for these analytes.
3 Method 8041 includes a dervatization technique followed by GC/ECD analysis, if interferences are encountered using GC/FID.
4 Methods 8280 and 8290 contain the extraction, cleanup, and determinative procedures for these analytes.

TABLE 2-39. DETERMINATIVE METHODS ORGANIC ANALYTES

Analyte Type	GC/MS Method	Specific GC Method	HPLC Method
Acid Extractable	8270		
Acrolein, Acrylonitrile, Acetonitrile	8260	8031 8033[1]	8315[2] 8316
Acrylamide	8260	8032	8316
Aniline and Selected Derivatives	8270	8131	
Aromatic Volatiles	8260	8021	
Base/Neutral Extractable	8270		8325[4]
Carbamates			8318, 8321
Chlorinated Herbicides	8270[3]	8151	8321
Chlorinated Hydrocarbons	8270	8121	
Dyes			8321
Explosives			8330, 8331, 8332
Formaldehyde			8315
Haloethers	8270	8111	
Halogenated Volatiles	8260	8011, 8021	
Nitroaromatics and Cyclic Ketones	8270	8091	8330[5]
Nitrosoamines	8270	8070	
Non-halogenated Volatiles	8260	8015	8315
Organochlorine Pesticides	8270[3]	8081	
Organophosphorus Pesticides	8270[3]	8141	8321
Phenols	8270	8041	
Petroleum Hydrocarbons		8015	
Phthalate Esters	8270	8061	
Polychlorinated Biphenyls	8270[3]	8082	
PCDDs and PCDFs	8280 8290		
Polynuclear Aromatic Hydrocarbons	8270	8100	8310
Volatile Organics	8260	8011, 8015, 8021, 8031, 8032, 8033	8315 8316

1 Of these analytes, Method 8033 is for acetonitrile only.
2 Of these analytes, Method 8315 is for acrolein only.
3 This method is an alternative confirmation method, not the method of choice.
4 Benzidines and related compounds.
5 Nitroaromatics (see "Explosives").

FIGURE 2-1
ORGANIC ANALYSIS OPTIONS FOR SOLID AND LIQUID MATRICES

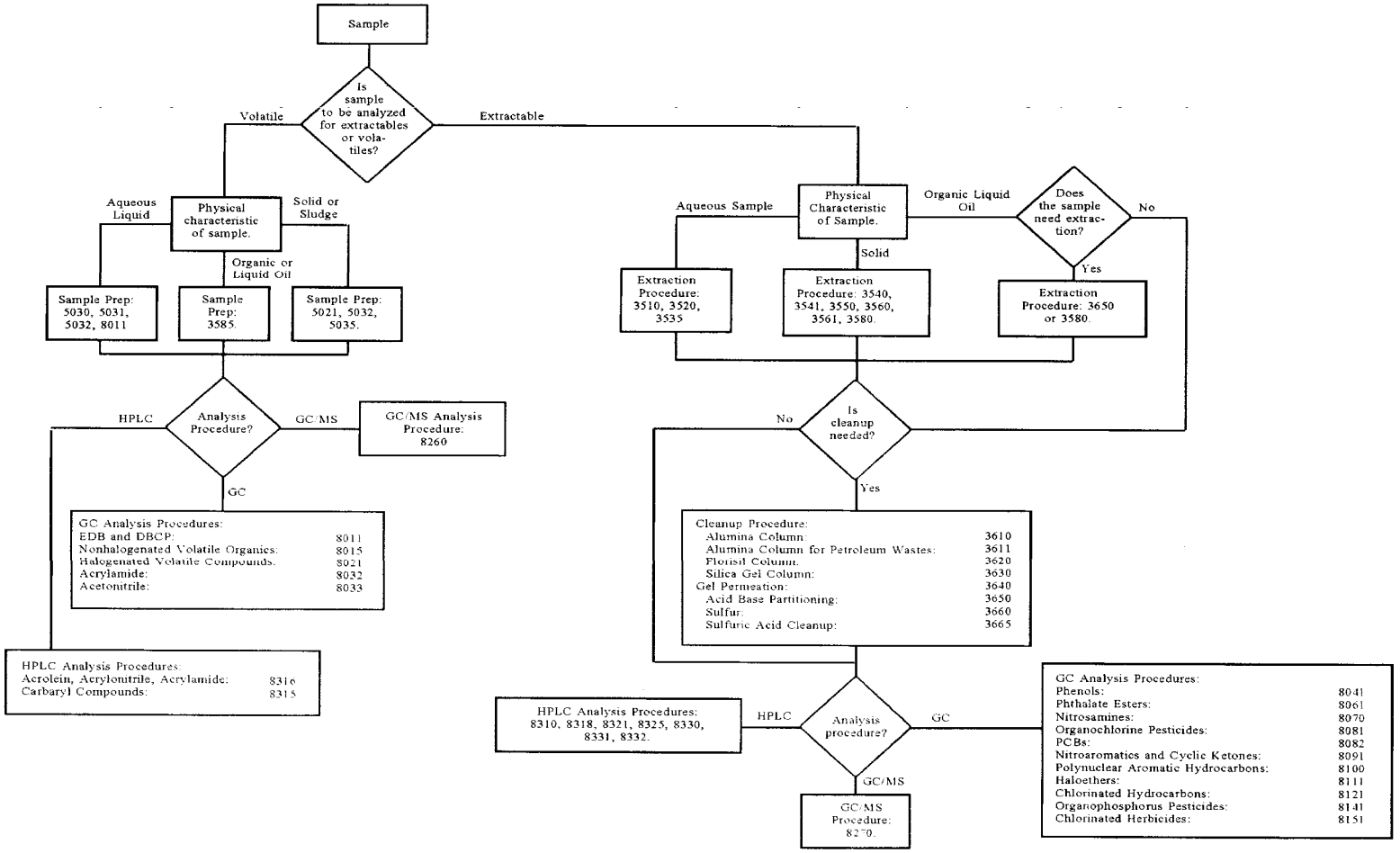


FIGURE 2-2
SCHEMATIC OF SEQUENCE TO DETERMINE
IF A WASTE IS HAZARDOUS BY CHARACTERISTIC

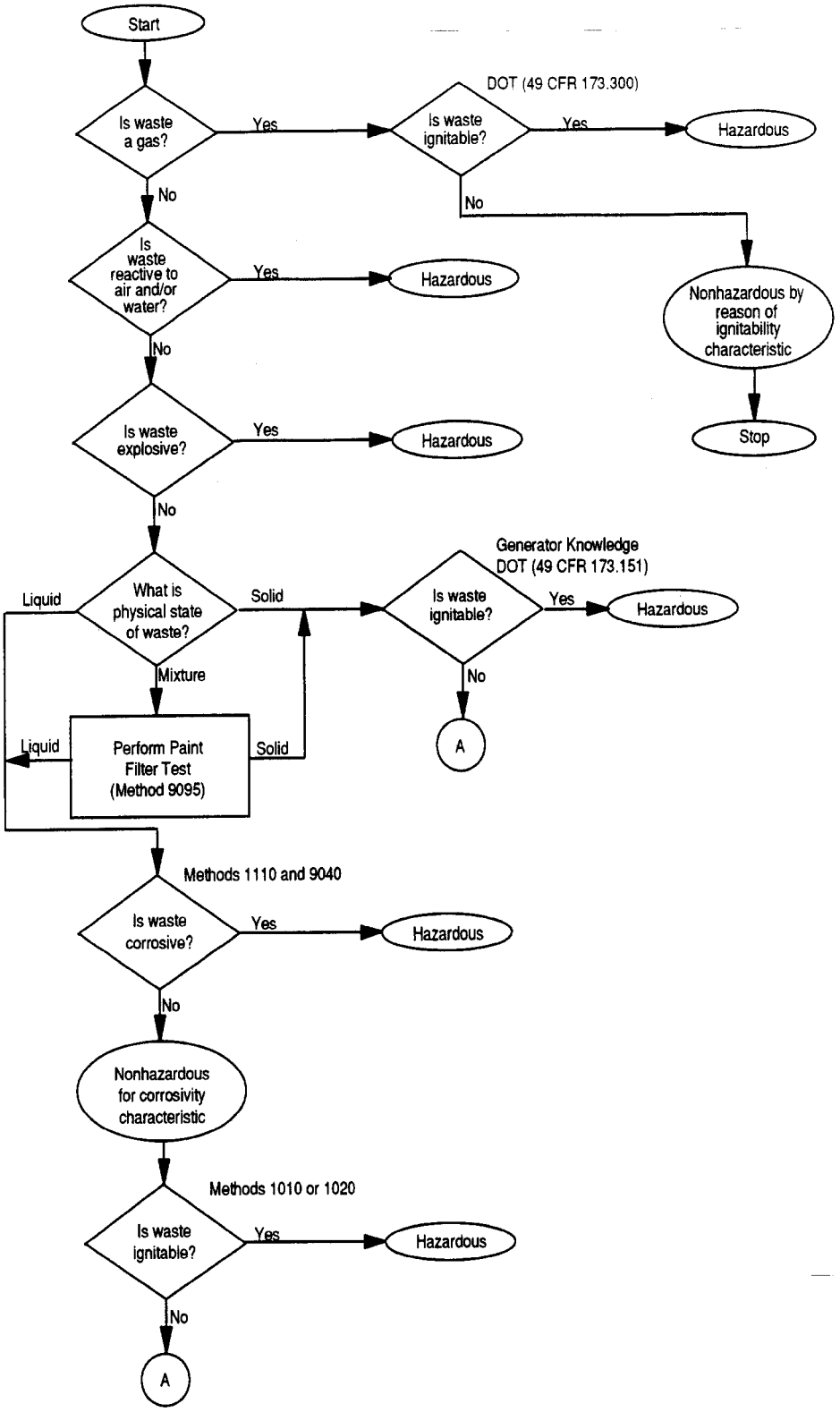


FIGURE 2-2
(Continued)

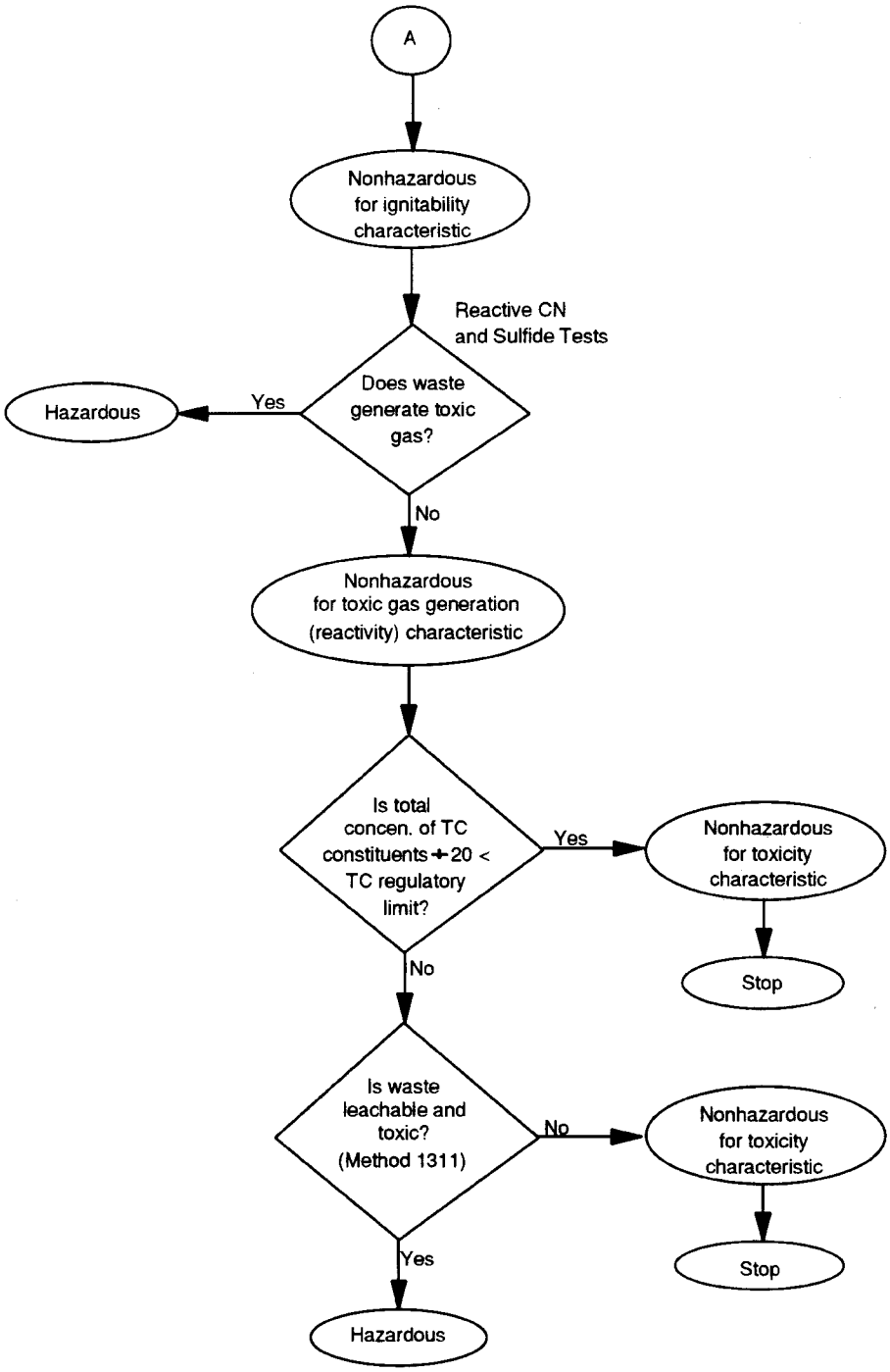
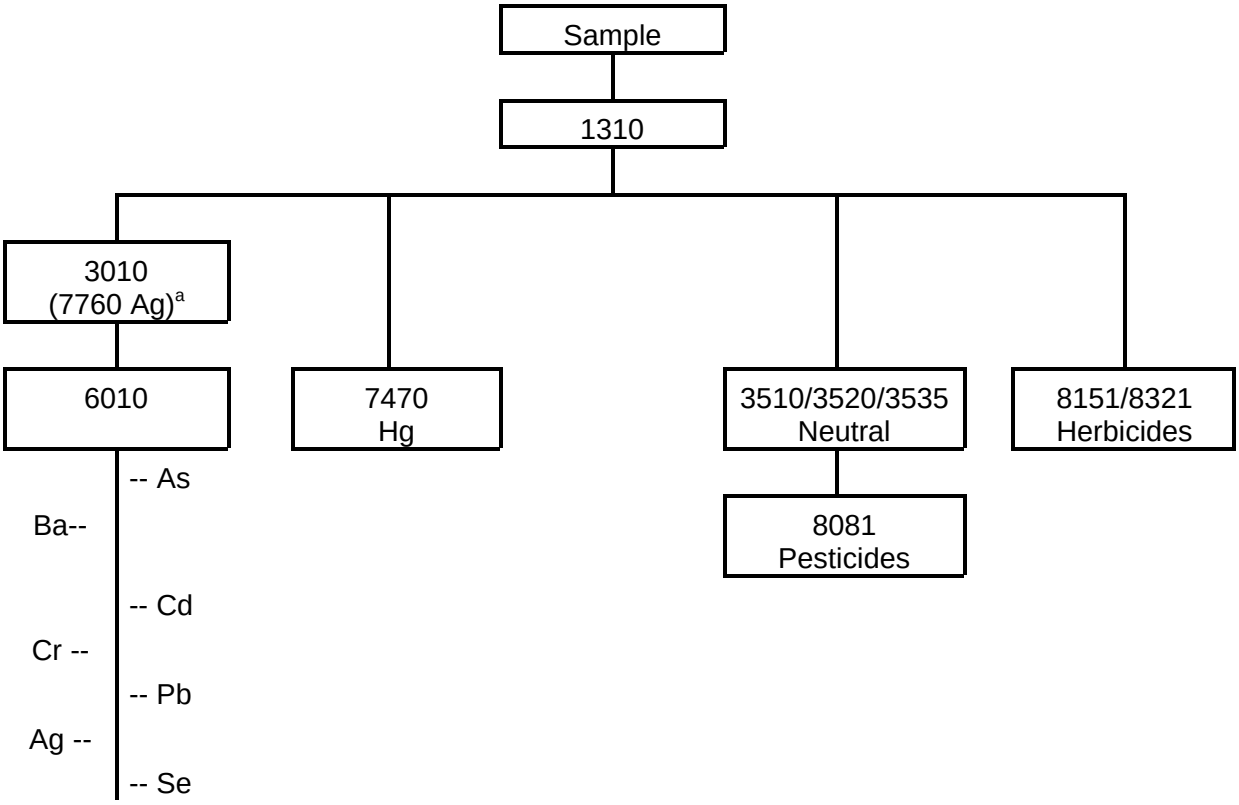
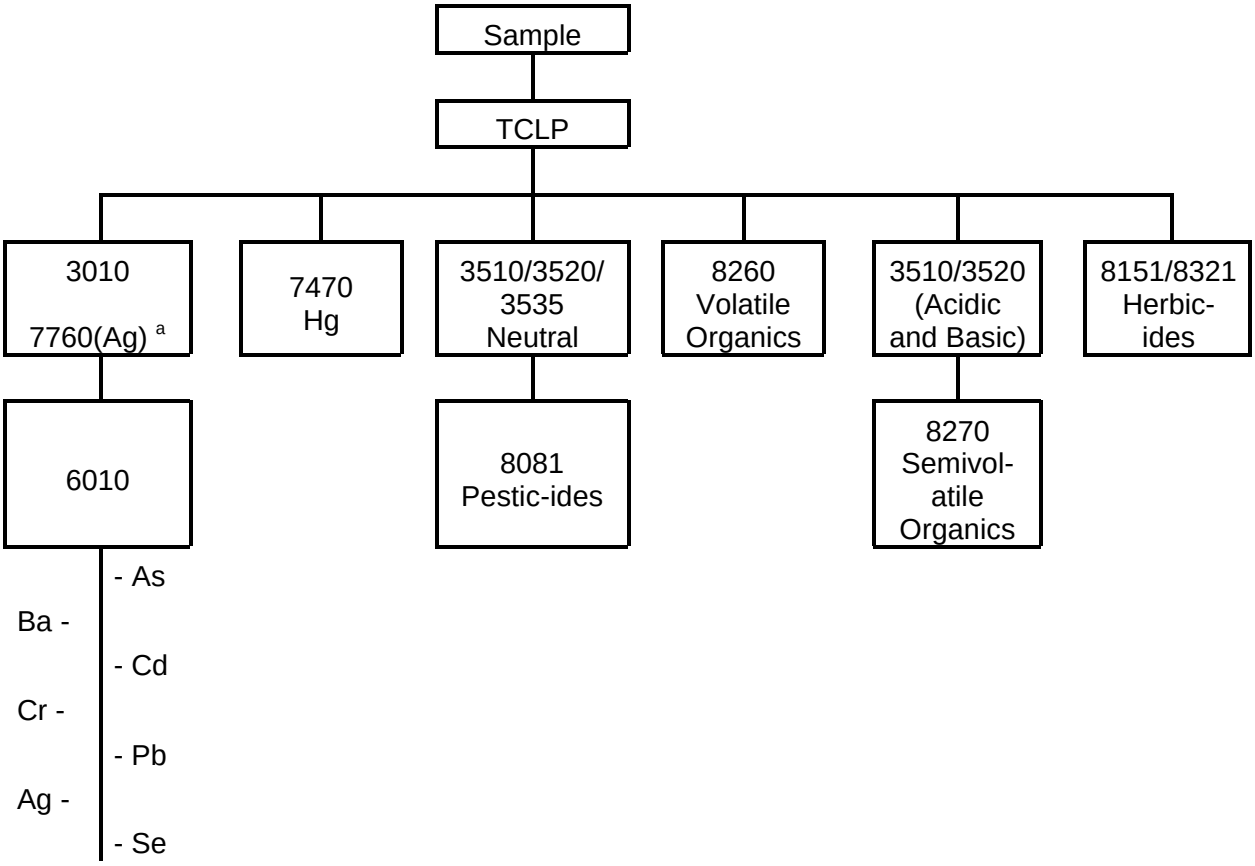


FIGURE 2-3A
EP



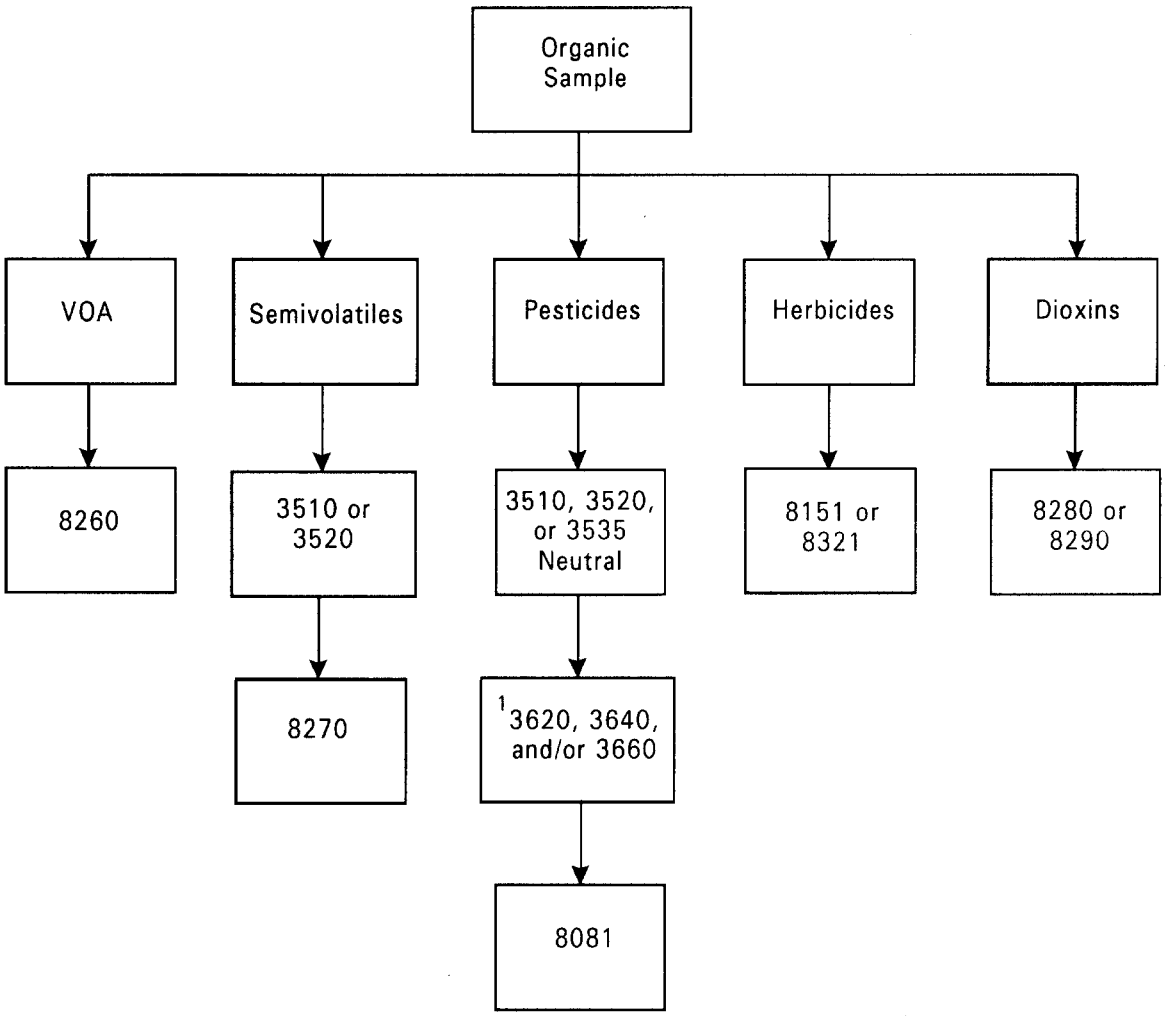
[a] The 7760 digestate may be analyzed using Method 6010.

FIGURE 2-3B
RECOMMENDED SW-846 METHODS OF ANALYSIS FOR TCLP LEACHATES



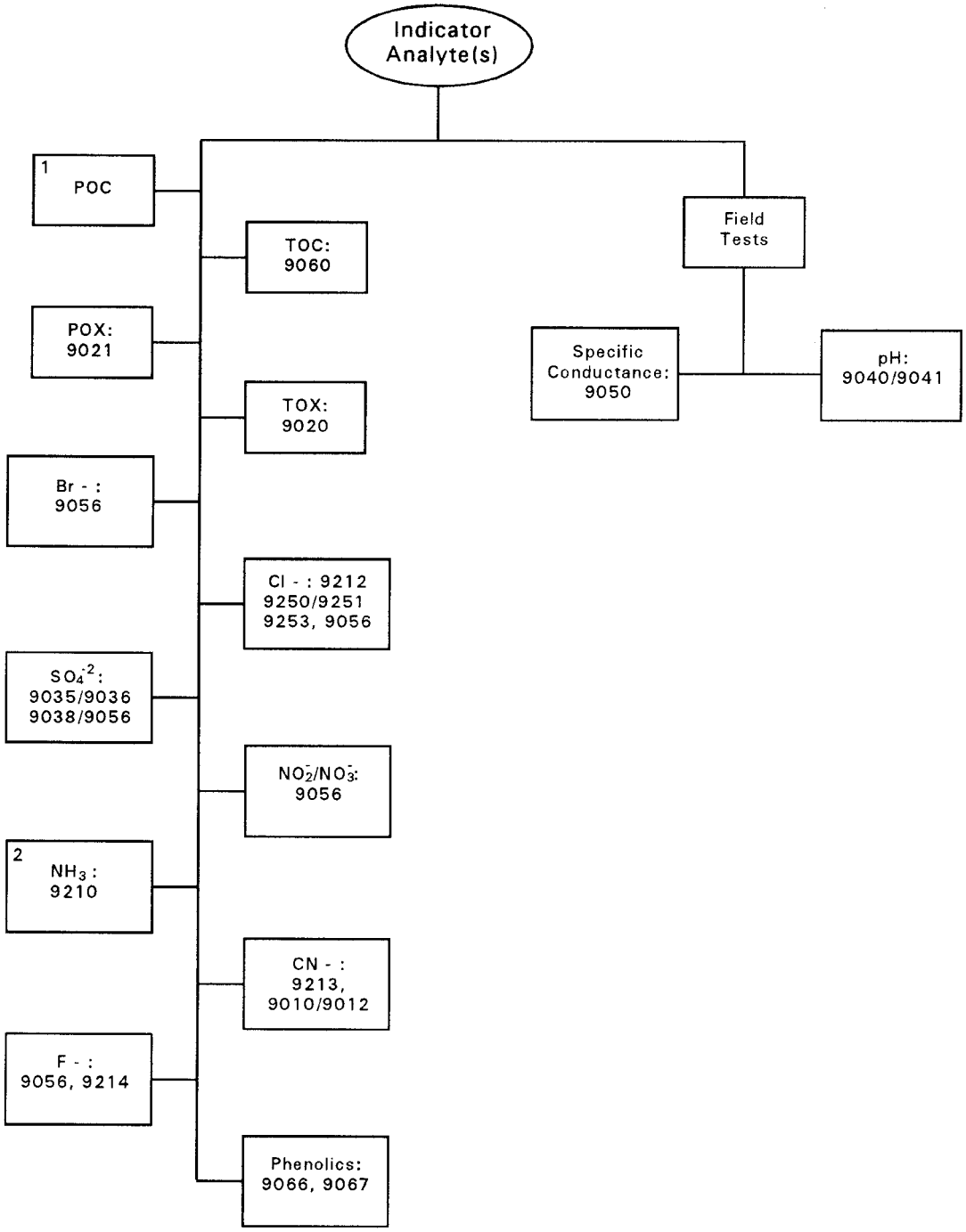
[a] The 7760 digestate may be analyzed using Method 6010.

FIGURE 2-4A.
GROUND WATER ANALYSIS: ORGANIC ANALYTES



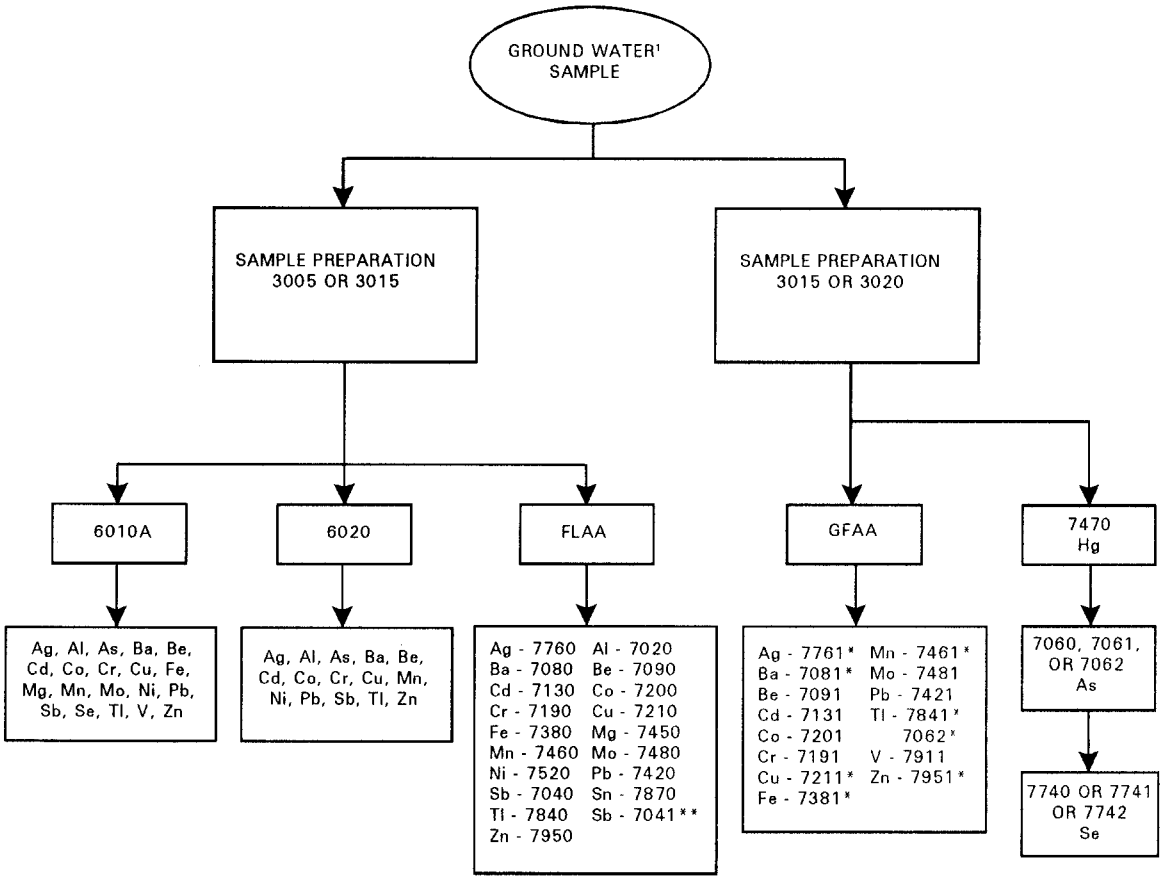
1 - Optional: Cleanup required only if interferences prevent analysis.

FIGURE 2-4B.
GROUND WATER ANALYSIS: INDICATOR ANALYTES



1 - Barcelona, 1984, (See Reference 1)
2 - Riggin, 1984, (See Reference 2)

FIGURE 2-4C.
GROUND WATER ANALYSIS: INORGANIC ANALYTES



* Follow the digestion procedures as detailed in the individual determinative methods.
** GFAA
[1] When analyzing for total dissolved metals, digestion is not necessary if the samples are filtered at the time of collection, and then acidified to the same concentration as the standards.

Annex 3

الملحق الثـــالث

CHAPTER THREE

INORGANIC ANALYTES

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

3.1 SAMPLING CONSIDERATIONS

3.1.1 Introduction

This manual contains procedures for the analysis of inorganic analytes in a variety of matrices. These methods are written as specific steps in the overall analysis scheme -- sample handling and preservation, sample digestion or preparation, and sample analysis for specific inorganic components. From these methods, the analyst must assemble a total analytical protocol which is appropriate for the sample to be analyzed and for the information required. This introduction discusses the options available in general terms, provides background information on the analytical techniques, and highlights some of the considerations to be made when selecting a total analysis protocol.

3.1.2 Definition of Terms

Optimum concentration range: A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating conditions employed.

Sensitivity: (a) Atomic Absorption: The concentration in milligrams of metal per liter that produces an absorption of 1%; (b) Inductively Coupled Plasma (ICP): The slope of the analytical curve, i.e., the functional relationship between emission intensity and concentration.

Method detection limit (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined from analysis of a sample in a given matrix containing the analyte which has been processed through the preparative procedure.

Total recoverable metals: The concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid (Method 3005).

Dissolved metals: The concentration of metals determined in a sample after the sample is filtered through a 0.45-µm filter (Method 3005).

Suspended metals: The concentration of metals determined in the portion of a sample that is retained by a 0.45-µm filter (Method 3005).

Total metals: The concentration of metals determined in a sample following digestion by Methods 3010, 3015, 3020, 3050, 3051, or 3052.

Instrument detection limit (IDL): The concentration equivalent to a signal due to the analyte which is equal to three times the standard deviation of a series of 7 replicate measurements of a reagent blank's signal at the same wavelength.

Interference check sample (ICS): A solution containing both interfering and analyte elements of known concentration that can be used to verify background and inter-element correction factors.

Initial calibration verification (ICV) standard: A certified or independently prepared solution used to verify the accuracy of the initial calibration. For ICP analysis, it must be run at each wavelength used in the analysis.

Continuing calibration verification (CCV): Used to assure calibration accuracy during each analysis run. It must be run for each analyte as described in the particular analytical method. At a minimum, it should be analyzed at the beginning of the run and after the last analytical sample. Its concentration should be at or near the mid-range levels of the calibration curve.

Calibration standards: A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve).

Linear dynamic range: The concentration range over which the analytical curve remains linear.

Method blank: A volume of reagent water processed through each sample preparation procedure.

Calibration blank: A volume of reagent water acidified with the same amounts of acids as were the standards and samples.

Laboratory control standard: A volume of reagent water spiked with known concentrations of analytes and carried through the preparation and analysis procedure as a sample. It is used to monitor loss/recovery values.

Method of standard addition (MSA): The standard-addition technique involves the use of the unknown and the unknown plus one or more known amounts of standard. See Method 7000, for detailed instructions.

Sample holding time: The storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are employed.

Check Standard: A solution containing a known concentration of analyte derived from externally prepared test materials. The check standard is obtained from a source external to the laboratory and is used to check laboratory performance.

3.1.3 Sample Handling and Preservation

Sample holding times, digestion volumes and suggested collection volumes are listed in Table 3-1. The sample volumes required depend upon the number of different digestion procedures necessary for analysis. This may be determined by the application of graphite-furnace atomic absorption spectrometry (GFAA), flame atomic absorption spectrometry (FLAA), inductively coupled argon plasma emission spectrometry (ICP), hydride-generation atomic absorption spectrometry (HGAA), inductively coupled plasma mass spectrometry (ICP-MS) or cold-vapor atomic absorption spectrometry (CVAA) techniques, each of which may require different digestion procedures. The indicated volumes in Table 3-1 refer to that recommended for the individual digestion procedures and to that recommended for sample collection volumes. In all cases for waste testing, representative sampling must be maintained.

In the determination of trace metals, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption, and (b) depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis require particular attention. The following cleaning treatment sequence has been determined to be adequate to minimize contamination in the sample bottle, whether borosilicate glass, linear polyethylene, polypropylene, or Teflon: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and reagent water.

NOTE: **Chromic acid should not be used to clean glassware**, especially if chromium is to be included in the analytical scheme. Commercial, non-chromate products (e.g., Nochromix) may be used in place of chromic acid if adequate cleaning is documented by an analytical quality control program. (Chromic acid should also not be used with plastic bottles.)

3.1.4 Safety

The toxicity or carcinogenicity of each reagent used in these methods has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in these methods. A reference file of material data-handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available. They are:

1. "Carcinogens - Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

2. "OSHA Safety and Health Standards, General Industry," 29 CFR 1910.

3. "Proposed OSHA Safety and Health Standards, Laboratories," Occupational Safety and Health Administration, 51 FR 26660, July 24, 1986.

4. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety.

TABLE 3-1.

SAMPLE HOLDING TIMES, RECOMMENDED DIGESTION VOLUMES AND RECOMMENDED COLLECTION VOLUMES FOR INORGANIC DETERMINATIONS IN AQUEOUS AND SOLID SAMPLES

Measurement	Digestion Volume. (mL)[a, c]	Collection Volume (mL)[a,c]	Treatment/ Preservative Holding Time[b]
Inorganic Analytes (except hexavalent chromium and mercury):			
Aqueous			
Total	100	600	HNO_3 to pH <2 6 months
Dissolved	100	600	Filter on site; HNO_3 to pH <2 6 months
Suspended	100	600	Filter on site 6 months
Solid			
Total	2 g	200 g	6 months
Hexavalent Chromium:			
Aqueous	100	400	24 hours Store at 4°± 2°C until analyzed
Solid	2.5 g	100 g	One month to extraction, 4 days after extraction Store at 4°± 2°C until analyzed
Mercury:			
Aqueous			
Total	100	400	HNO_3 to pH <2 28 days
Dissolved	100	400	Filter; HNO_3 to pH <2 28 days
Solid			
Total	0.2 g	200 g	28 days Store at 4°± 2°C until analyzed

[a] Unless stated otherwise.

[b] Either glass or plastic containers may be used.

[c] Any sample volume reduction from the reference method's instructions must be made in the exact proportion as described in the method and representative sampling must be maintained.

3.2 SAMPLE PREPARATION METHODS

The methods in SW-846 for sample digestion or preparation are as follows[1]:

Method 3005 prepares ground water and surface water samples for total recoverable and dissolved metal determinations by FLAA, ICP-AES, or ICP-MS. The unfiltered or filtered sample is heated with dilute HCl and HNO_3 prior to metal determination.

Method 30l0 prepares waste samples for total recoverable metal determinations by FLAA, ICP-AES, or ICP-MS. The samples are vigorously digested with nitric acid followed by dilution with hydrochloric acid. The method is applicable to aqueous samples, EP and mobility-procedure extracts.

Method 3015 prepares aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for total recoverable metal determinations by FLAA, GFAA, ICP-AES, or ICP-MS. Nitric acid is added to the sample in a Teflon digestion vessel and heated in a microwave unit prior to metals determination.

Method 3020 prepares waste samples for total recoverable metals determinations by furnace GFAA or ICP-MS. The samples are vigorously digested with nitric acid followed by dilution with nitric acid. The method is applicable to aqueous samples, EP and mobility-procedure extracts.

Method 3031 prepares waste oils, oil sludges, tars, waxes, paints, paint sludges and other viscous petroleum products for analysis by FLAA, GFAA, and ICP-AES. The samples are vigorously digested with nitric acid, sulfuric acid, hydrochloric acid, and potassium permanganate prior to analysis.

Method 3040 prepares oily waste samples for determination of soluble metals by FLAA, GFAA, and ICP-AES methods. The samples are dissolved and diluted in organic solvent prior to analysis. The method is applicable to the organic extract in the oily waste EP procedure and other samples high in oil, grease, or wax content.

Method 3050 prepares waste samples for total recoverable metals determinations by FLAA and ICP-AES, or GFAA and ICP-MS depending on the options chosen. The samples are vigorously digested in nitric acid and hydrogen peroxide followed by dilution with either nitric or hydrochloric acid. The method is applicable to soils, sludges, and solid waste samples.

Method 3051 prepares sludges, sediments, soils and oils for total recoverable metal determinations by FLAA, GFAA, ICP-AES or ICP-MS. Nitric acid is added to the representative sample in a fluorocarbon digestion vessel and heated in a microwave unit prior to metals determination.

Method 3052 prepares siliceous and organically based matrices including ash, biological tissue, oil, oil contaminated soil, sediment, sludge, and soil for total analysis by FLAA, CVAA, GFAA, ICP-AES, and ICP-MS. Nitric acid and hydrofluoric acid are added to a representative sample in a fluorocarbon digestion vessel and heated in a microwave unit prior to analysis.

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[1] Please note that chlorine is an interferant in ICP-MS analyses and its use should be discouraged except when absolutely necessary.

Prior to employing the above methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

3.3 METHODS FOR DETERMINATION OF INORGANIC ANALYTES

This section of the manual contains seven analytical techniques for trace inorganic analyte determinations: inductively coupled argon plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), direct-aspiration or flame atomic absorption spectrometry (FLAA), graphite-furnace atomic absorption spectrometry (GFAA), hydride-generation atomic absorption spectrometry (HGAA), cold-vapor atomic absorption spectrometry (CVAA), and several procedures for hexavalent chromium analysis. Each of these is briefly discussed below in terms of advantages, disadvantages, and cautions for analysis of wastes.

ICP's primary advantage is that it allows simultaneous or rapid sequential determination of many elements in a short time. The primary disadvantage of ICP is background radiation from other elements and the plasma gases. Although all ICP instruments utilize high-resolution optics and back-ground correction to minimize these interferences, analysis for traces of inorganic analytes in the presence of a large excess of a single analyte is difficult. Examples would be traces of inorganic analytes in an alloy or traces of metals in a limed (high calcium) waste. ICP and Flame AA have comparable detection limits (within a factor of 4) except that ICP exhibits greater sensitivity for refractories (Al, Ba, etc.). Furnace AA, in general, will exhibit lower detection limits than either ICP or FLAA. Detection limits are drastically improved when ICP-MS is used. In general ICP-MS exhibits greater sensitivity than either GFAA or FLAA for most elements. The greatest disadvantage of ICP-MS is isobaric elemental interferences. These are caused by different elements forming atomic ions with the same nominal mass-to-charge ratio. Mathematical correction for interfering ions can minimize these interferences.

Flame AAS (FLAA) direct aspiration determinations, as opposed to ICP, are normally completed as single element analyses and are relatively free of interelement spectral interferences. Either a nitrous-oxide/acetylene or air/acetylene flame is used as an energy source for dissociating the aspirated sample into the free atomic state, making analyte atoms available for absorption of light. In the analysis of some elements, the temperature or type of flame used is critical. If the proper flame and analytical conditions are not used, chemical and ionization interferences can occur.

Graphite Furnace AAS (GFAA) replaces the flame with an electrically heated graphite furnace. The furnace allows for gradual heating of the sample aliquot in several stages. Thus, the processes of dissolution, drying, decomposition of organic and inorganic molecules and salts, and formation of atoms which must occur in a flame or ICP in a few milliseconds may be allowed to occur over a much longer time period and at controlled temperatures in the furnace. This allows an experienced analyst to remove unwanted matrix components by using temperature programming and/or matrix modifiers. The major advantage of this technique is that it affords extremely low detection limits. It is the easiest to perform on relatively clean samples. Because this technique is so sensitive, interferences can be a real problem; finding the optimum combination of digestion, heating times and temperatures, and matrix modifiers can be a challenge for complex matrices.

Hydride AA utilizes a chemical reduction to reduce and separate arsenic or selenium selectively from a sample digestate. The technique therefore has the advantage of being able to isolate these two elements from complex samples which may cause interferences for other analytical procedures. Significant interferences have been reported when any of the following is present: 1) easily reduced metals (Cu, Ag, Hg); 2) high concentrations of transition metals (>200 mg/L); 3) oxidizing agents (oxides of nitrogen) remaining following sample digestion.

Cold-Vapor AA uses a chemical reduction to reduce mercury selectively. The procedure is extremely sensitive but is subject to interferences from some volatile organics, chlorine, and sulfur compounds.

Prior to employing the above methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

Annex 4

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CHAPTER ONE
TABLE OF CONTENTS

TABLE OF CONTENTS
(continued)

CHAPTER ONE
QUALITY CONTROL

1.0 INTRODUCTION

It is the goal of the U.S. Environmental Protection Agency's (EPA's) quality assurance (QA) program to ensure that all data be scientifically valid, defensible, and of known precision and accuracy. The data should be of sufficient known quality to withstand scientific and legal challenge relative to the use for which the data are obtained. The QA program is management's tool for achieving this goal.

For RCRA analyses, the recommended minimum requirements for a QA program and the associated quality control (QC) procedures are provided in this chapter.

The data acquired from QC procedures are used to estimate the quality of analytical data, to determine the need for corrective action in response to identified deficiencies, and to interpret results after corrective action procedures are implemented. Method-specific QC procedures are incorporated in the individual methods since they are not applied universally.

A total program to generate data of acceptable quality should include both a QA component, which encompasses the management procedures and controls, as well as an operational day-to-day QC component. This chapter defines fundamental elements of such a data collection program. Data collection efforts involve:

1. design of a project plan to achieve the data quality objectives (DQOs);

2. implementation of the project plan; and

3. assessment of the data to determine if the DQOs are met.

The project plan may be a sampling and analysis plan or a waste analysis plan if it covers the QA/QC goals of the Chapter, or it may be a Quality Assurance Project Plan as described later in this chapter.

This chapter identifies the minimal QC components that should be used in the performance of sampling and analyses, including the QC information which should be documented. Guidance is provided to construct QA programs for field and laboratory work conducted in support of the RCRA program.

2.0 QA PROJECT PLAN

It is recommended that all projects which generate environment-related data in support of RCRA have a QA Project Plan (QAPjP) or equivalent. In some instances, a sampling and analysis plan or a waste analysis plan may be equivalent if it covers all of the QA/QC goals outlined in this chapter. In addition, a separate QAPjP need not be prepared for routine analyses or

activities where the procedures to be followed are described in a Standard Operating Procedures manual or similar document and include the elements of a QAPjP. These documents should be available and referenced in the documentation and/or records for the analysis activities. The term "QAPjP" in this chapter refers to any of these QA/QC documents.

The QAPjP should detail the QA/QC goals and protocols for a specific data collection activity. The QAPjP sets forth a plan for sampling and analysis activities that will generate data of a quality commensurate with their intended use. QAPjP elements should include a description of the project and its objectives; a statement of the DQOs of the project; identification of those involved in the data collection and their responsibilities and authorities; reference to (or inclusion of) the specific sample collection and analysis procedures that will be followed for all aspects of the project; enumeration of QC procedures to be followed; and descriptions of all project documentation. Additional elements should be included in the QAPjP if needed to address all quality related aspects of the data collection project. Elements should be omitted only when they are inappropriate for the project or when absence of those elements will not affect the quality of data obtained for the project (see reference 1).

The role and importance of DQOs and project documentation are discussed below in Sections 2.1 through 2.6. Management and organization play a critical role in determining the effectiveness of a QA/QC program and ensuring that all required procedures are followed. Section 2.7 discusses the elements of an organization's QA program that have been found to ensure an effective program. Field operations and laboratory operations (along with applicable QC procedures) are discussed in Sections 3 and 4, respectively.

2.1 DATA QUALITY OBJECTIVES

Data quality objectives (DQOs) for the data collection activity describe the overall level of uncertainty that a decision-maker is willing to accept in results derived from environmental data. This uncertainty is used to specify the quality of the measurement data required, usually in terms of objectives for precision, bias, representativeness, comparability and completeness. The DQOs should be defined prior to the initiation of the field and laboratory work. The field and laboratory organizations performing the work should be aware of the DQOs so that their personnel may make informed decisions during the course of the project to attain those DQOs. More detailed information on DQOs is available from the U.S. EPA Quality Assurance Management Staff (QAMS) (see references 2 and 4).

2.2 PROJECT OBJECTIVES

A statement of the project objectives and how the objectives are to be attained should be concisely stated and sufficiently detailed to permit clear understanding by all parties involved in the data collection effort. This

includes a statement of what problem is to be solved and the information required in the process. It also includes appropriate statements of the DQOs (i.e., the acceptable level of uncertainty in the information).

2.3 SAMPLE COLLECTION

Sampling procedures, locations, equipment, and sample preservation and handling requirements should be specified in the QAPjP. Further details on quality assurance procedures for field operations are described in Section 3 of this chapter. The OSW is developing policies and procedures for sampling in a planned revision of Chapter Nine of this manual. Specific procedures for groundwater sampling are provided in Chapter Eleven of this manual.

2.4 ANALYSIS AND TESTING

Analytes and properties of concern, analytical and testing procedures to be employed, required detection limits, and requirements for precision and bias should be specified. All applicable regulatory requirements and the project DQOs should be considered when developing the specifications. Further details on the procedures for analytical operations are described in Section 4 of this chapter.

2.5 QUALITY CONTROL

The quality assurance program should address both field and laboratory activities. Quality control procedures should be specified for estimating the precision and bias of the data. Recommended minimum requirements for QC samples have been established by EPA and should be met in order to satisfy recommended minimum criteria for acceptable data quality. Further details on procedures for field and laboratory operations are described in Sections 3 and 4, respectively, of this chapter.

2.6 PROJECT DOCUMENTATION

Documents should be prepared and maintained in conjunction with the data collection effort. Project documentation should be sufficient to allow review of all aspects of the work being performed. The QAPjP discussed in Sections 3 and 4 is one important document that should be maintained.

The length of storage time for project records should comply with regulatory requirements, organizational policy, or project requirements, whichever is more stringent. It is recommended that documentation be stored for three years from submission of the project final report.

Documentation should be secured in a facility that adequately addresses/minimizes its deterioration for the length of time that it is to be

retained. A system allowing for the expedient retrieval of information should exist.

Access to archived information should be controlled to maintain the integrity of the data. Procedures should be developed to identify those individuals with access to the data.

2.7 ORGANIZATION PERFORMING FIELD OR LABORATORY OPERATIONS

Proper design and structure of the organization facilitates effective and efficient transfer of information and helps to prevent important procedures from being overlooked.

The organizational structure, functional responsibilities, levels of authority, job descriptions, and lines of communication for all project activities should be established and documented. One person may cover more than one organizational function. Each project participant should have a clear understanding of his or her duties and responsibilities and the relationship of those responsibilities to the overall data collection effort.

The management of each organization participating in a project involving data collection activities should establish that organization's operational and QA policies. This information should be documented in the QAPjP. The management should ensure that (1) the appropriate methodologies are followed as documented in the QAPjPs; (2) personnel clearly understand their duties and responsibilities; (3) each staff member has access to appropriate project documents; (4) any deviations from the QAPjP are communicated to the project management and documented; and (5) communication occurs between the field, laboratory, and project management, as specified in the QAPjP. In addition, each organization should ensure that their activities do not increase the risk to humans or the environment at or about the project location. Certain projects may require specific policies or a Health and Safety Plan to provide this assurance.

The management of the participating field or laboratory organization should establish personnel qualifications and training requirements for the project. Each person participating in the project should have the education, training, technical knowledge, and experience, or a combination thereof, to enable that individual to perform assigned functions. Training should be provided for each staff member as necessary to perform their functions properly. Personnel qualifications should be documented in terms of education, experience, and training, and periodically reviewed to ensure adequacy to current responsibilities.

Each participating field organization or laboratory organization should have a designated QA function (i.e., a team or individual trained in QA) to monitor operations to ensure that the equipment, personnel, activities, procedures, and documentation conform with the QAPjP. To the extent possible, the QA monitoring function should be entirely separate from, and independent of,

personnel engaged in the work being monitored. The QA function should be responsible for the QA review.

2.7.1 Performance Evaluation

Performance evaluation studies are used to measure the performance of the laboratory on unknown samples. Performance evaluation samples are typically submitted to the laboratory as blind samples by an independent outside source. The results are compared to predetermined acceptance limits. Performance evaluation samples can also be submitted to the laboratory as part of the QA function during internal assessment of laboratory performance. Records of all performance evaluation studies should be maintained by the laboratory. Problems identified through participation in performance evaluation studies should be immediately investigated and corrected.

2.7.2 Internal Assessment by QA Function

Personnel performing field and laboratory activities are responsible for continually monitoring individual compliance with the QAPjP. The QA function should review procedures, results and calculations to determine compliance with the QAPjP. The results of this internal assessment should be reported to management with requirements for a plan to correct observed deficiencies.

2.7.3 External Assessment

The field and laboratory activities may be reviewed by personnel external to the organization. Such an assessment is an extremely valuable method for identifying overlooked problems. The results of the external assessment should be submitted to management with requirements for a plan to correct observed deficiencies.

2.7.4 On-Site Evaluation

On-site evaluations may be conducted as part of both internal and external assessments. The focus of an on-site evaluation is to evaluate the degree of conformance of project activities with the applicable QAPjP. On-site evaluations may include, but are not limited to, a complete review of facilities, staff, training, instrumentation, procedures, methods, sample collection, analyses, QA policies and procedures related to the generation of environmental data. Records of each evaluation should include the date of the evaluation, location, the areas reviewed, the person performing the evaluation, findings and problems, and actions recommended and taken to resolve problems. Any problems identified that are likely to affect data integrity should be brought immediately to the attention of management.

2.7.4.1 Field Activities

The review of field activities should be conducted by one or more persons knowledgeable in the activities being reviewed and include evaluating, at a minimum, the following subjects:

Completeness of Field Reports -- This review determines whether all requirements for field activities in the QAPjP have been fulfilled, that complete records exist for each field activity, and that the procedures specified in the QAPjP have been implemented. Emphasis on field documentation will help assure sample integrity and sufficient technical information to recreate each field event. The results of this completeness check should be documented, and environmental data affected by incomplete records should be identified.

Identification of Valid Samples -- This review involves interpretation and evaluation of the field records to detect problems affecting the representativeness of environmental samples. Examples of items that might indicate potentially invalid samples include improper well development, improperly screened wells, instability of pH or conductivity, and collection of volatiles near internal combustion engines. The field records should be evaluated against the QAPjP and SOPs. The reviewer should document the sample validity and identify the environmental data associated with any poor or incorrect field work.

Correlation of Field Test Data -- This review involves comparing any available results of field measurements obtained by more than one method. For example, surface geophysical methods should correlate with direct methods of site geologic characterization such as lithologic logs constructed during drilling operations.

Identification of Anomalous Field Test Data -- This review identifies any anomalous field test data. For example, a water temperature for one well that is 5 degrees higher than any other well temperature in the same aquifer should be noted. The reviewer should evaluate the impact of anomalous field measurement results on the associated environmental data.

Validation of Field Analyses -- This review validates and documents all data from field analysis that are generated *in situ* or from a mobile laboratory as specified in Section 2.7.4.2. The reviewer should document whether the QC checks meet the acceptance criteria, and whether corrective actions were taken for any analysis performed when acceptance criteria were exceeded.

2.7.4.2 Laboratory Activities

The review of laboratory data should be conducted by one or more persons knowledgeable in laboratory activities and include evaluating, at a minimum, the following subjects:

Completeness of Laboratory Records -- This review determines whether: (1) all samples and analyses required by the QAPjP have been processed, (2) complete records exist for each analysis and the associated QC samples, and that (3) the procedures specified in the QAPjP have been implemented. The results of the completeness check should be documented, and environmental data affected by incomplete records should be identified.

Evaluation of Data with Respect to Detection and Quantitation Limits -- This review compares analytical results to required quantitation limits. Reviewers should document instances where detection or quantitation limits exceed regulatory limits, action levels, or target concentrations specified in the QAPjP.

Evaluation of Data with Respect to Control Limits -- This review compares the results of QC and calibration check samples to control criteria. Corrective action should be implemented for data not within control limits. The reviewer should check that corrective action reports, and the results of reanalysis, are available. The review should determine whether samples associated with out-of-control QC data are identified in a written record of the data review, and whether an assessment of the utility of such analytical results is recorded.

Review of Holding Time Data -- This review compares sample holding times to those required by the QAPjP, and notes all deviations.

Review of Performance Evaluation (PE) Results -- PE study results can be helpful in evaluating the impact of out-of-control conditions. This review documents any recurring trends or problems evident in PE studies and evaluates their effect on environmental data.

Correlation of Laboratory Data -- This review determines whether the results of data obtained from related laboratory tests, e.g., Purgeable Organic Halides (POX) and Volatile Organics, are documented, and whether the significance of any differences is discussed in the reports.

2.7.5 QA Reports

There should be periodic reporting of pertinent QA/QC information to the project management to allow assessment of the overall effectiveness of the QA program. There are three major types of QA reports to project management:

Periodic Report on Key QA Activities -- Provides summary of key QA activities during the period, stressing measures that are being taken to improve data quality; describes significant quality problems observed and corrective actions taken; reports information regarding any changes in certification/accreditation status; describes involvement in resolution of quality issues with clients or agencies; reports any QA organizational changes; and provides notice of the distribution of revised documents controlled by the QA organization (i.e., procedures).

Report on Measurement Quality Indicators -- Includes the assessment of QC data gathered over the period, the frequency of analyses repeated due to unacceptable QC performance, and, if possible, the reason for the unacceptable performance and corrective action taken.

Reports on QA Assessments -- Includes the results of the assessments and the plan for correcting identified deficiencies; submitted immediately

following any internal or external on-site evaluation or upon receipt of the results of any performance evaluation studies.

3.0 FIELD OPERATIONS

The field operations should be conducted in such a way as to provide reliable information that meets the DQOs. To achieve this, certain minimal policies and procedures should be implemented. The OSW is considering revisions of Chapter Nine and Eleven of this manual. Supplemental information and guidance is available in the RCRA Ground-Water Monitoring Technical Enforcement Guidance Document (TEGD) (Reference 3). The project documentation should contain the information specified below.

3.1 FIELD LOGISTICS

The QAPjP should describe the type(s) of field operations to be performed and the appropriate area(s) in which to perform the work. The QAPjP should address ventilation, protection from extreme weather and temperatures, access to stable power, and provision for water and gases of required purity.

Whenever practical, the sampling site facilities should be examined prior to the start of work to ensure that all required items are available. The actual area of sampling should be examined to ensure that trucks, drilling equipment, and personnel have adequate access to the site.

The determination as to whether sample shipping is necessary should be made during planning for the project. This need is established by evaluating the analyses to be performed, sample holding times, and location of the site and the laboratory. Shipping or transporting of samples to a laboratory should be done within a timeframe such that recommended holding times are met.

Samples should be packaged, labelled, preserved (e.g., preservative added, iced, etc.), and documented in an area which is free of contamination and provides for secure storage. The level of custody and whether sample storage is needed should be addressed in the QAPjP.

Storage areas for solvents, reagents, standards, and reference materials should be adequate to preserve their identity, concentration, purity, and stability prior to use.

Decontamination of sampling equipment may be performed at the location where sampling occurs, prior to going to the sampling site, or in designated areas near the sampling site. Project documentation should specify where and how this work is accomplished. If decontamination is to be done at the site, water and solvents of appropriate purity should be available. The method of accomplishing decontamination, including the required materials, solvents, and water purity should be specified.

During the sampling process and during on-site or in situ analyses, waste materials are sometimes generated. The method for storage and disposal of these waste materials that complies with applicable local, state and Federal regulations should be specified. Adequate facilities should be provided for the collection and storage of all wastes, and these facilities should be operated so as to minimize environmental contamination. Waste storage and disposal facilities should comply with applicable federal, state, and local regulations.

The location of long-term and short-term storage for field records, and the measures to ensure the integrity of the data should be specified.

3.2 EQUIPMENT/INSTRUMENTATION

The equipment, instrumentation, and supplies at the sampling site should be specified and should be appropriate to accomplish the activities planned. The equipment and instrumentation should meet the requirements of specifications, methods, and procedures as specified in the QAPjP.

3.3 OPERATING PROCEDURES

The QAPjP should describe or make reference to all field activities that may affect data quality. For routinely performed activities, standard operating procedures (SOPs) are often prepared to ensure consistency and to save time and effort in preparing QAPjPs. Any deviation from an established procedure during a data collection activity should be documented. The procedures should be available for the indicated activities, and should include, at a minimum, the information described below.

3.3.1 Sample Management

The numbering and labeling system, chain-of-custody procedures, and how the samples are to be tracked from collection to shipment or receipt by the laboratory should be specified. Sample management procedures should also specify the holding times, volumes of sample required by the laboratory, required preservatives, and shipping requirements.

3.3.2 Reagent/Standard Preparation

The procedures describing how to prepare standards and reagents should be specified. Information concerning specific grades of materials used in reagent and standard preparation, appropriate glassware and containers for preparation and storage, and labeling and record keeping for stocks and dilutions should be included.

3.3.3 Decontamination

The procedures describing decontamination of field equipment before and during the sample collection process should be specified. These procedures

should include cleaning materials used, the order of washing and rinsing with the cleaning materials, requirements for protecting or covering cleaned equipment, and procedures for disposing of cleaning materials.

3.3.4 Sample Collection

The procedures describing how the sampling operations are actually performed in the field should be specified. A simple reference to standard methods is not sufficient, unless a procedure is performed exactly as described in the published method. Methods from source documents published by the EPA, American Society for Testing and Materials, U.S. Department of the Interior, National Water Well Association, American Petroleum Institute, or other recognized organizations with appropriate expertise should be used, if possible. The procedures for sample collection should include at least the following:

- Applicability of the procedure,
- Equipment required,
- Detailed description of procedures to be followed in collecting the samples,
- Common problems encountered and corrective actions to be followed, and
- Precautions to be taken.

3.3.5 Field Measurements

The procedures describing all methods used in the field to determine a chemical or physical parameter should be described in detail. The procedures should address criteria from Section 4, as appropriate.

3.3.6 Equipment Calibration And Maintenance

The procedures describing how to ensure that field equipment and instrumentation are in working order should be specified. These describe calibration procedures and schedules, maintenance procedures and schedules, maintenance logs, and service arrangements for equipment. Calibration and maintenance of field equipment and instrumentation should be in accordance with manufacturers' specifications or applicable test specifications and should be documented.

3.3.7 Corrective Action

The procedures describing how to identify and correct deficiencies in the sample collection process should be specified. These should include specific steps to take in correcting deficiencies such as performing additional decontamination of equipment, resampling, or additional training of field personnel. The procedures should specify that each corrective action should be documented with a description of the deficiency and the corrective action taken,

and should include the person(s) responsible for implementing the corrective action.

3.3.8 Data Reduction and Validation

The procedures describing how to compute results from field measurements and to review and validate these data should be specified. They should include all formulas used to calculate results and procedures used to independently verify that field measurement results are correct.

3.3.9 Reporting

The procedures describing the process for reporting the results of field activities should be specified.

3.3.10 Records Management

The procedures describing the means for generating, controlling, and archiving project-specific records and field operations records should be specified. These procedures should detail record generation and control and the requirements for record retention, including type, time, security, and retrieval and disposal authorities.

Project-specific records relate to field work performed for a project. These records may include correspondence, chain-of-custody records, field notes, all reports issued as a result of the work, and procedures used.

Field operations records document overall field operations and may include equipment performance and maintenance logs, personnel files, general field procedures, and corrective action reports.

3.3.11 Waste Disposal

The procedures describing the methods for disposal of waste materials resulting from field operations should be specified.

3.4 FIELD QA AND QC REQUIREMENTS

The QAPjP should describe how the following elements of the field QC program will be implemented.

3.4.1 Control Samples

Control samples are QC samples that are introduced into a process to monitor the performance of the system. Control samples, which may include blanks (e.g., trip, equipment, and laboratory), duplicates, spikes, analytical standards, and reference materials, can be used in different phases of the data collection process beginning with sampling and continuing through transportation, storage, and analysis.

Each day of sampling, at least one field duplicate and one equipment rinsate should be collected for each matrix sampled. If this frequency is not appropriate for the sampling equipment and method, then the appropriate changes should be clearly identified in the QAPjP. When samples are collected for volatile organic analysis, a trip blank is also recommended for each day that samples are collected. In addition, for each sampling batch (20 samples of one matrix type), enough volume should be collected for at least one sample so as to allow the laboratory to prepare one matrix spike and either one matrix duplicate or one matrix spike duplicate for each analytical method employed. This means that the following control samples are recommended:

- Field duplicate (one per day per matrix type)
- Equipment rinsate (one per day per matrix type)
- Trip blank (one per day, volatile organics only)
- Matrix spike (one per batch [20 samples of each matrix type])
- Matrix duplicate or matrix spike duplicate (one per batch)

Additional control samples may be necessary in order to assure data quality to meet the project-specific DQOs.

3.4.2 Acceptance Criteria

Procedures should be in place for establishing acceptance criteria for field activities described in the QAPjP. Acceptance criteria may be qualitative or quantitative. Field events or data that fall outside of established acceptance criteria may indicate a problem with the sampling process that should be investigated.

3.4.3 Deviations

All deviations from plan should be documented as to the extent of, and reason for, the deviation. Any activity not performed in accordance with procedures or QAPjPs is considered a deviation from plan. Deviations from plan may or may not affect data quality.

3.4.4 Corrective Action

Errors, deficiencies, deviations, certain field events, or data that fall outside established acceptance criteria should be investigated. In some instances, corrective action may be needed to resolve the problem and restore proper functioning to the system. The investigation of the problem and any subsequent corrective action taken should be documented.

3.4.5 Data Handling

All field measurement data should be reduced according to protocols described or referenced in the QAPjP. Computer programs used for data reduction should be validated before use and verified on a regular basis. All information used in the calculations should be recorded to enable reconstruction of the final result at a later date.

Data should be reported in accordance with the requirements of the end-user as described in the QAPjP.

3.5 QUALITY ASSURANCE REVIEW

The QA Review consists of internal and external assessments to ensure that QA/QC procedures are in use and to ensure that field staff conform to these procedures. QA review should be conducted as deemed appropriate and necessary.

3.6 FIELD RECORDS

Records provide the direct evidence and support for the necessary technical interpretations, judgments, and discussions concerning project activities. These records, particularly those that are anticipated to be used as evidentiary data, should directly support current or ongoing technical studies and activities and should provide the historical evidence needed for later reviews and analyses. Records should be legible, identifiable, and retrievable and protected against damage, deterioration, or loss. The discussion in this section (3.6) outlines recommended procedures for record keeping. Organizations which conduct field sampling should develop appropriate record keeping procedures which satisfy relevant technical and legal requirements.

Field records generally consist of bound field notebooks with prenumbered pages, sample collection forms, personnel qualification and training forms, sample location maps, equipment maintenance and calibration forms, chain-of-custody forms, sample analysis request forms, and field change request forms. All records should be written in indelible ink.

Procedures for reviewing, approving, and revising field records should be clearly defined, with the lines of authority included. It is recommended that all documentation errors should be corrected by drawing a single line through the error so it remains legible and should be initialed by the responsible individual, along with the date of change. The correction should be written adjacent to the error.

Records should include (but are not limited to) the following:

Calibration Records & Traceability of Standards/Reagents -- Calibration is a reproducible reference point to which all sample measurements can be correlated. A sound calibration program should include provisions for documentation of frequency, conditions, standards, and records reflecting the calibration history of a measurement system. The accuracy of the calibration standards is important because all data will be in reference to the standards used. A program for verifying and documenting the accuracy of all working standards against primary grade standards should be routinely followed.

Sample Collection -- To ensure maximum utility of the sampling effort and resulting data, documentation of the sampling protocol, as performed in the field, is essential. It is recommended that sample collection records contain, at a minimum, the names of persons conducting the activity, sample number, sample location, equipment used, climatic conditions, documentation of adherence to protocol, and unusual observations. The actual sample collection record is usually one of the following: a bound field notebook with prenumbered pages, a pre-printed form, or digitized information on a computer tape or disc.

Chain-of-Custody Records -- The chain-of-custody involving the possession of samples from the time they are obtained until they are disposed or shipped off-site should be documented as specified in the QAPjP and should include the following information: (1) the project name; (2) signatures of samplers; (3) the sample number, date and time of collection, and grab or composite sample designation; (4) signatures of individuals involved in sample transfer; and (5) if applicable, the air bill or other shipping number.

Maps and Drawings -- Project planning documents and reports often contain maps. The maps are used to document the location of sample collection points and monitoring wells and as a means of presenting environmental data. Information used to prepare maps and drawings is normally obtained through field surveys, property surveys, surveys of monitoring wells, aerial photography or photogrammetric mapping. The final, approved maps and/or drawings should have a revision number and date and should be subject to the same controls as other project records.

QC Samples -- Documentation for generation of QC samples, such as trip and equipment rinsate blanks, duplicate samples, and any field spikes should be maintained.

Deviations -- All deviations from procedural documents and the QAPjP should be recorded in the site logbook.

Reports -- A copy of any report issued and any supporting documentation should be retained.

4.0 LABORATORY OPERATIONS

The laboratory should conduct its operations in such a way as to provide reliable information. To achieve this, certain minimal policies and procedures should be implemented.

4.1 FACILITIES

The QAPjP should address all facility-related issues that may impact project data quality. Each laboratory should be of suitable size and

construction to facilitate the proper conduct of the analyses. Adequate bench space or working area per analyst should be provided. The space requirement per analyst depends on the equipment or apparatus that is being utilized, the number of samples that the analyst is expected to handle at any one time, and the number of operations that are to be performed concurrently by a single analyst. Other issues to be considered include, but are not limited to, ventilation, lighting, control of dust and drafts, protection from extreme temperatures, and access to a source of stable power.

Laboratories should be designed so that there is adequate separation of functions to ensure that no laboratory activity has an adverse effect on the analyses. The laboratory may require specialized facilities such as a perchloric acid hood or glovebox.

Separate space for laboratory operations and appropriate ancillary support should be provided, as needed, for the performance of routine and specialized procedures.

As necessary to ensure secure storage and prevent contamination or misidentification, there should be adequate facilities for receipt and storage of samples. The level of custody required and any special requirements for storage such as refrigeration should be described in planning documents.

Storage areas for reagents, solvents, standards, and reference materials should be adequate to preserve their identity, concentration, purity, and stability.

Adequate facilities should be provided for the collection and storage of all wastes, and these facilities should be operated so as to minimize environmental contamination. Waste storage and disposal facilities should comply with applicable federal, state, and local regulations.

The location of long-term and short-term storage of laboratory records and the measures to ensure the integrity of the data should be specified.

4.2 EQUIPMENT/INSTRUMENTATION

Equipment and instrumentation should meet the requirements and specifications of the specific test methods and other procedures as specified in the QAPjP. The laboratory should maintain an equipment/instrument description list that includes the manufacturer, model number, year of purchase, accessories, and any modifications, updates, or upgrades that have been made.

4.3 OPERATING PROCEDURES

The QAPjP should describe or make reference to all laboratory activities that may affect data quality. For routinely performed activities, SOPs are often prepared to ensure consistency and to save time and effort in preparing QAPjPs.

Any deviation from an established procedure during a data collection activity should be documented. It is recommended that procedures be available for the indicated activities, and include, at a minimum, the information described below.

4.3.1 Sample Management

The procedures describing the receipt, handling, scheduling, and storage of samples should be specified.

Sample Receipt and Handling -- These procedures describe the precautions to be used in opening sample shipment containers and how to verify that chain-of-custody has been maintained, examine samples for damage, check for proper preservatives and temperature, and log samples into the laboratory sample streams.

Sample Scheduling -- These procedures describe the sample scheduling in the laboratory and includes procedures used to ensure that holding time requirements are met.

Sample Storage -- These procedures describe the storage conditions for all samples, verification and documentation of daily storage temperature, and how to ensure that custody of the samples is maintained while in the laboratory.

4.3.2 Reagent/Standard Preparation

The procedures describing how to prepare standards and reagents should be specified. Information concerning specific grades of materials used in reagent and standard preparation, appropriate glassware and containers for preparation and storage, and labeling and recordkeeping for stocks and dilutions should be included.

4.3.3 General Laboratory Techniques

The procedures describing all essentials of laboratory operations that are not addressed elsewhere should be specified. These techniques should include, but are not limited to, glassware cleaning procedures, operation of analytical balances, pipetting techniques, and use of volumetric glassware.

4.3.4 Test Methods

Procedures for test methods describing how the analyses are actually performed in the laboratory should be specified. A simple reference to standard methods is not sufficient, unless the analysis is performed exactly as described in the published method. Whenever methods from SW-846 are not appropriate, recognized methods from source documents published by the EPA, American Public Health Association (APHA), American Society for Testing and Materials (ASTM), the National Institute for Occupational Safety and Health (NIOSH), or other recognized organizations with appropriate expertise should be used, if possible.

The documentation of the actual laboratory procedures for analytical methods should include the following:

Sample Preparation and Analysis Procedures -- These include applicable holding time, extraction, digestion, or preparation steps as appropriate to the method; procedures for determining the appropriate dilution to analyze; and any other information required to perform the analysis accurately and consistently.

Instrument Standardization -- This includes concentration(s) and frequency of analysis of calibration standards, linear range of the method, and calibration acceptance criteria.

Sample Data -- This includes recording requirements and documentation including sample identification number, analyst, data verification, date of analysis and verification, and computational method(s).

Precision and Bias -- This includes all analytes for which the method is applicable and the conditions for use of this information.

Detection and Reporting Limits -- This includes all analytes in the method.

Test-Specific QC -- This describes QC activities applicable to the specific test and references any applicable QC procedures.

4.3.5 Equipment Calibration and Maintenance

The procedures describing how to ensure that laboratory equipment and instrumentation are in working order should be specified. These procedures include calibration procedures and schedules, maintenance procedures and schedules, maintenance logs, service arrangements for all equipment, and spare parts available in-house. Calibration and maintenance of laboratory equipment and instrumentation should be in accordance with manufacturers' specifications or applicable test specifications and should be documented.

4.3.6 QC

The type, purpose, and frequency of QC samples to be analyzed in the laboratory and the acceptance criteria should be specified. Information should include the applicability of the QC sample to the analytical process, the statistical treatment of the data, and the responsibility of laboratory staff and management in generating and using the data. Further details on development of project-specific QC protocols are described in Section 4.4.

4.3.7 Corrective Action

The procedures describing how to identify and correct deficiencies in the analytical process should be specified. These should include specific steps to take in correcting the deficiencies such as preparation of new standards and

reagents, recalibration and restandardization of equipment, reanalysis of samples, or additional training of laboratory personnel in methods and procedures. The procedures should specify that each corrective action should be documented with a description of the deficiency and the corrective action taken, and should include the person(s) responsible for implementing the corrective action.

4.3.8 Data Reduction and Validation

The procedures describing how to review and validate the data should be specified. They should include procedures for computing and interpreting the results from QC samples, and independent procedures to verify that the analytical results are reported correctly. In addition, routine procedures used to monitor precision and bias, including evaluations of reagent, equipment rinsate, and trip blanks, calibration standards, control samples, duplicate and matrix spike samples, and surrogate recovery, should be detailed in the procedures. More detailed validation procedures should be performed when required in the contract or QAPjP.

4.3.9 Reporting

The procedures describing the process for reporting the analytical results should be specified.

4.3.10 Records Management

The procedures describing the means for generating, controlling, and archiving laboratory records should be specified. The procedures should detail record generation and control, and the requirements for record retention, including type, time, security, and retrieval and disposal authorities.

Project-specific records may include correspondence, chain-of-custody records, request for analysis, calibration data records, raw and finished analytical and QC data, data reports, and procedures used.

Laboratory operations records may include laboratory notebooks, instrument performance logs and maintenance logs in bound notebooks with prenumbered pages; laboratory benchsheets; software documentation; control charts; reference material certification; personnel files; laboratory procedures; and corrective action reports.

4.3.11 Waste Disposal

The procedures describing the methods for disposal of chemicals including standard and reagent solutions, process waste, and samples should be specified.

4.4 LABORATORY QA AND QC PROCEDURES

The QAPjP should describe how the following required elements of the laboratory QC program are to be implemented.

4.4.1 Method Proficiency

Procedures should be in place for demonstrating proficiency with each analytical method routinely used in the laboratory. These should include procedures for demonstrating the precision and bias of the method as performed by the laboratory and procedures for determining the method detection limit (MDL). All terminology, procedures and frequency of determinations associated with the laboratory's establishment of the MDL and the reporting limit should be well-defined and well-documented. Documented precision, bias, and MDL information should be maintained for all methods performed in the laboratory.

4.4.2 Control Limits

Procedures should be in place for establishing and updating control limits for analysis. Control limits should be established to evaluate laboratory precision and bias based on the analysis of control samples. Typically, control limits for bias are based on the historical mean recovery plus or minus three standard deviation units, and control limits for precision range from zero (no difference between duplicate control samples) to the historical mean relative percent difference plus three standard deviation units. Procedures should be in place for monitoring historical performance and should include graphical (control charts) and/or tabular presentations of the data.

4.4.3 Laboratory Control Procedures

Procedures should be in place for demonstrating that the laboratory is in control during each data collection activity. Analytical data generated with laboratory control samples that fall within prescribed limits are judged to be generated while the laboratory was in control. Data generated with laboratory control samples that fall outside the established control limits are judged to be generated during an "out-of-control" situation. These data are considered suspect and should be repeated or reported with qualifiers.

Laboratory Control Samples -- Laboratory control samples should be analyzed for each analytical method when appropriate for the method. A laboratory control sample consists of either a control matrix spiked with analytes representative of the target analytes or a certified reference material.

Laboratory control sample(s) should be analyzed with each batch of samples processed to verify that the precision and bias of the analytical process are within control limits. The results of the laboratory control sample(s) are compared to control limits established for both precision and bias to determine usability of the data.

Method Blank -- When appropriate for the method, a method blank should be analyzed with each batch of samples processed to assess contamination

levels in the laboratory. Guidelines should be in place for accepting or rejecting data based on the level of contamination in the blank.

Procedures should be in place for documenting the effect of the matrix on method performance. When appropriate for the method, there should be at least one matrix spike and either one matrix duplicate or one matrix spike duplicate per analytical batch. Additional control samples may be necessary to assure data quality to meet the project-specific DQOs.

Matrix-Specific Bias -- Procedures should be in place for determining the bias of the method due to the matrix. These procedures should include preparation and analysis of matrix spikes, selection and use of surrogates for organic methods, and the method of standard additions for metal and inorganic methods. When the concentration of the analyte in the sample is greater than 0.1%, no spike is necessary.

Matrix-Specific Precision -- Procedures should be in place for determining the precision of the method for a specific matrix. These procedures should include analysis of matrix duplicates and/or matrix spike duplicates. The frequency of use of these techniques should be based on the DQO for the data collection activity.

Matrix-Specific Detection Limit -- Procedures should be in place for determining the MDL for a specific matrix type (e.g., wastewater treatment sludge, contaminated soil, etc).

4.4.4 Deviations

Any activity not performed in accordance with laboratory procedures or QAPjPs is considered a deviation from plan. All deviations from plan should be documented as to the extent of, and reason for, the deviation.

4.4.5 Corrective Action

Errors, deficiencies, deviations, or laboratory events or data that fall outside of established acceptance criteria should be investigated. In some instances, corrective action may be needed to resolve the problem and restore proper functioning to the analytical system. The investigation of the problem and any subsequent corrective action taken should be documented.

4.4.6 Data Handling

Data resulting from the analyses of samples should be reduced according to protocols described in the laboratory procedures. Computer programs used for data reduction should be validated before use and verified on a regular basis. All information used in the calculations (e.g., raw data, calibration files, tuning records, results of standard additions, interference check results, and blank- or background-correction protocols) should be recorded in order to enable reconstruction of the final result at a later date. Information on the preparation of the sample (e.g., weight or volume of sample used, percent dry

weight for solids, extract volume, dilution factor used) should also be maintained in order to enable reconstruction of the final result at a later date.

All data should be reviewed by a second analyst or supervisor according to laboratory procedures to ensure that calculations are correct and to detect transcription errors. Spot checks should be performed on computer calculations to verify program validity. Errors detected in the review process should be referred to the analyst(s) for corrective action. Data should be reported in accordance with the requirements of the end-user. It is recommended that the supporting documentation include at a minimum:

- Laboratory name and address.
- Sample information (including unique sample identification, sample collection date and time, date of sample receipt, and date(s) of sample preparation and analysis).
- Analytical results reported with an appropriate number of significant figures.
- Detection limits that reflect dilutions, interferences, or correction for equivalent dry weight.
- Method reference.
- Appropriate QC results (correlation with sample batch should be traceable and documented).
- Data qualifiers with appropriate references and narrative on the quality of the results.

4.5 QUALITY ASSURANCE REVIEW

The QA review consists of internal and external assessments to ensure that QA/QC procedures are in use and to ensure that laboratory staff conform to these procedures. QA review should be conducted as deemed appropriate and necessary.

4.6 LABORATORY RECORDS

Records provide the direct evidence and support for the necessary technical interpretations, judgements, and discussions concerning project activities. These records, particularly those that are anticipated to be used as evidentiary data, should directly support technical studies and activities, and provide the historical evidence needed for later reviews and analyses. Records should be legible, identifiable, and retrievable, and protected against damage, deterioration, or loss. The discussion in this section (4.6) outlines recommended procedures for record keeping. Organizations which conduct field

sampling should develop appropriate record keeping procedures which satisfy relevant technical and legal requirements.

Laboratory records generally consist of bound notebooks with prenumbered pages, personnel qualification and training forms, equipment maintenance and calibration forms, chain-of-custody forms, sample analysis request forms, and analytical change request forms. All records should be written in indelible ink.

Procedures for reviewing, approving, and revising laboratory records should be clearly defined, with the lines of authority included. Any documentation errors should be corrected by drawing a single line through the error so that it remains legible and should be initialed by the responsible individual, along with the date of change. The correction is written adjacent to the error.

Strip-chart recorder printouts should be signed by the person who performed the instrumental analysis. If corrections need to be made in computerized data, a system parallel to the corrections for handwritten data should be in place.

Records of sample management should be available to permit the re-creation of an analytical event for review in the case of an audit or investigation of a dubious result.

Laboratory records should include, at least, the following:

Operating Procedures -- Procedures should be available to those performing the task outlined. Any revisions to laboratory procedures should be written, dated, and distributed to all affected individuals to ensure implementation of changes. Areas covered by operating procedures are given in Sections 3.3 and 4.3.

Quality Assurance Plans -- The QAPjP should be on file.

Equipment Maintenance Documentation -- A history of the maintenance record of each system serves as an indication of the adequacy of maintenance schedules and parts inventory. As appropriate, the maintenance guidelines of the equipment manufacturer should be followed. When maintenance is necessary, it should be documented in either standard forms or in logbooks. Maintenance procedures should be clearly defined and written for each measurement system and required support equipment.

Proficiency -- Proficiency information on all compounds reported should be maintained and should include (1) precision; (2) bias; (3) method detection limits; (4) spike recovery, where applicable; (5) surrogate recovery, where applicable; (6) checks on reagent purity, where applicable; and (7) checks on glassware cleanliness, where applicable.

Calibration Records & Traceability of Standards/Reagents -- Calibration is a reproducible reference point to which all sample measurements can be correlated. A sound calibration program should include provisions for documenting frequency, conditions, standards, and records reflecting the

calibration history of a measurement system. The accuracy of the calibration standards is important because all data will be in reference to the standards used. A program for verifying and documenting the accuracy and traceability of all working standards against appropriate primary grade standards or the highest quality standards available should be routinely followed.

Sample Management -- All required records pertaining to sample management should be maintained and updated regularly. These include chain-of-custody forms, sample receipt forms, and sample disposition records.

Original Data -- The raw data and calculated results for all samples should be maintained in laboratory notebooks, logs, benchsheets, files or other sample tracking or data entry forms. Instrumental output should be stored in a computer file or a hardcopy report.

QC Data -- The raw data and calculated results for all QC and field samples and standards should be maintained in the manner described in the preceding paragraph. Documentation should allow correlation of sample results with associated QC data. Documentation should also include the source and lot numbers of standards for traceability. QC samples include, but are not limited to, control samples, method blanks, matrix spikes, and matrix spike duplicates.

Correspondence -- Project correspondence can provide evidence supporting technical interpretations. Correspondence pertinent to the project should be kept and placed in the project files.

Deviations -- All deviations from procedural and planning documents should be recorded in laboratory notebooks. Deviations from QAPjPs should be reviewed and approved by the authorized personnel who performed the original technical review or by their designees.

Final Report -- A copy of any report issued and any supporting documentation should be retained.

5.0 DEFINITIONS

The following terms are defined for use in this document:

ACCURACY — The closeness of agreement between an observed value and an accepted reference value. When applied to a set of observed values, accuracy will be a combination of a random component and of a common systematic error (or bias) component.

BATCH: — A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit (see Section 3.4.1 for field

samples and Section 4.4.3 for laboratory samples). For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

BIAS: The deviation due to matrix effects of the measured value (x_s - x_u) from a known spiked amount. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of contaminant spiked into a sample (matrix spike). Thus, the bias (B) due to matrix effects based on a matrix spike is calculated as:

$$B = (x_s - x_u) - K$$

where:

x_s = measured value for spiked sample,
x_u = measured value for unspiked sample, and
K = known value of the spike in the sample.

Using the following equation yields the percent recovery (%R).

$$\%R = 100\ (x_s - x_u)/\ K$$

BLANK: see Equipment Rinsate, Method Blank, Trip Blank.

CONTROL SAMPLE: A QC sample introduced into a process to monitor the performance of the system.

DATA QUALITY OBJECTIVES (DQOs): A statement of the overall level of uncertainty that a decision-maker is willing to accept in results derived from environmental data (see reference 2, EPA/QAMS, July 16, 1986). This is qualitatively distinct from quality measurements such as precision, bias, and detection limit.

DATA VALIDATION: The process of evaluating the available data against the project DQOs to make sure that the objectives are met. Data validation may be very rigorous, or cursory, depending on project DQOs. The available data reviewed will include analytical results, field QC data and lab QC data, and may also include field records.

DUPLICATE: see Matrix Duplicate, Field Duplicate, Matrix Spike Duplicate.

EQUIPMENT BLANK: see Equipment Rinsate.

EQUIPMENT RINSATE: A sample of analyte-free media which has been used to

	rinse the sampling equipment. It is collected after completion of decontamination and prior to sampling. This blank is useful in documenting adequate decontamination of sampling equipment.
ESTIMATED QUANTITATION LIMIT (EQL):	The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected as the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs in SW-846 are provided for guidance and may not always be achievable.
FIELD DUPLICATES:	Independent samples which are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently. These duplicates are useful in documenting the precision of the sampling process.
LABORATORY CONTROL SAMPLE:	A known matrix spiked with compound(s) representative of the target analytes. This is used to document laboratory performance.
MATRIX:	The component or substrate (e.g., surface water, drinking water) which contains the analyte of interest.
MATRIX DUPLICATE:	An intralaboratory split sample which is used to document the precision of a method in a given sample matrix.
MATRIX SPIKE:	An aliquot of sample spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix.
MATRIX SPIKE DUPLICATES:	Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.
METHOD BLANK:	An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank should be carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

For a method blank to be acceptable for use with the accompanying samples, the concentration in the blank of any analyte of concern should not be higher than the highest of either:

(1)The method detection limit, or

(2)Five percent of the regulatory limit for that analyte, or

(3)Five percent of the measured concentration in the sample.

METHOD DETECTION LIMIT (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte.

For operational purposes, when it is necessary to determine the MDL in the matrix, the MDL should be determined by multiplying the appropriate one-sided 99% t-statistic by the standard deviation obtained from a minimum of three analyses of a matrix spike containing the analyte of interest at a concentration three to five times the estimated MDL, where the t-statistic is obtained from standard references or the table below.

No. of samples:	t-statistic
3	6.96
4	4.54
5	3.75
6	3.36
7	3.14
8	3.00
9	2.90
10	2.82

Estimate the MDL as follows:
Obtain the concentration value that corresponds to:

a) an instrument signal/noise ratio within the range of 2.5 to 5.0, or

b) the region of the standard curve where there is a significant change in sensitivity (i.e., a break in the slope of the standard curve).

Determine the variance (S^2) for each analyte as follows:

$$s^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n}(x_i - \bar{x})^2\right]$$

where x_i = the ith measurement of the variable x and $\bar{x}$ = the average value of x;

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$$

Determine the standard deviation (s) for each analyte as follows:

$$s = (S^2)^{1/2}$$

Determine the MDL for each analyte as follows:

$$MDL = t_{(n-1,\ \alpha = .99)}(s)$$

where $t_{(n-1,\ \alpha = .99)}$ is the one-sided t-statistic appropriate for the number of samples used to determine (s), at the 99 percent level.

ORGANIC-FREE REAGENT WATER:

For volatiles, all references to water in the methods refer to water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free deionized water. Organic-free reagent water may also be prepared by boiling water for 15 minutes and, subsequently, while maintaining the temperature at 90°C, bubbling a contaminant-free inert gas through the water for 1 hour.

For semivolatiles and nonvolatiles, all references to water in the methods refer to water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free deionized water.

PRECISION:

The agreement among a set of replicate measurements

without assumption of knowledge of the true value. Precision is estimated by means of duplicate/replicate analyses. These samples should contain concentrations of analyte above the MDL, and may involve the use of matrix spikes. The most commonly used estimates of precision are the relative standard deviation (RSD) or the coefficient of variation (CV),

$$RSD = CV = 100\ S/\bar{x},$$

where:
x = the arithmetic mean of the x_i measurements, and S = variance; and the relative percent difference (RPD) when only two samples are available.

$$RPD = 100\ [(x_1 - x_2)/\{(x_1 + x_2)/2\}].$$

PROJECT: Single or multiple data collection activities that are related through the same planning sequence.

QUALITY ASSURANCE PROJECT PLAN (QAPjP): An orderly assemblage of detailed procedures designed to produce data of sufficient quality to meet the data quality objectives for a specific data collection activity.

RCRA: The Resource Conservation and Recovery Act.

REAGENT BLANK: See Method Blank.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

SPLIT SAMPLES: Aliquots of sample taken from the same container and analyzed independently. In cases where aliquots of samples are impossible to obtain, field duplicate samples should be taken for the matrix duplicate analysis. These are usually taken after mixing or compositing and are used to document intra- or interlaboratory precision.

STANDARD ADDITION: The practice of adding a known amount of an analyte to a sample immediately prior to analysis. It is typically used to evaluate interferences.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

SURROGATE: An organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples.

TRIP BLANK: A sample of analyte-free media taken from the laboratory to the sampling site and returned to the laboratory unopened. A trip blank is used to document contamination attributable to shipping and field handling procedures. This type of blank is useful in documenting contamination of volatile organics samples.

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INDEX

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* Definition of term.

الكـيمـياء غير العضوية المتقدمة

خطة الدرس- المادة المقدمة

Advanced Inorganic Chemistry

Lesson Plan -Presentation

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Deutsche Gesellschaft für Technische Zusammenarbeit - GTZ
Water and Wastewater Management Programme
GTZ Project No. 06.2006.3

المحتويات

أولا: نظرة عامة على البرنامج التدريبى التحاليل العضوية في المياه (التحاليل الكيميائية- أسس استخدام أجهزة القياس المستخدمة - التحكم في جودة ودقة النتائج)

1. الهدف العام للدورة التدريبية
2. المجموعة المستهدفة
3. عدد المتدربين
4. منهجية التدريب
5. مساعدات التدريب
6. قائمة الدورات التدريبية
7. مكان التدريب و طريقة الجلوس بجلسات التدريب

ثانيا: خطة التدريس بالدورة التدريبية التحاليل العضوية في المياه (التحاليل الكيميائية- التحكم في جودة ودقة النتائج)

1. أهداف الدورة
2. موضوعات الدورة
3. مدة الدورة
4. البرنامج الزمنى للدورة

أولا: نظرة عامة على البرنامج التدريبى التحاليل العضوية في المياه (التحاليل الكيميائية - التحكم في جودة ودقة النتائج)

1. الهدف العام للدورة التدريبية

نظراً لخطورة الملوثات والعضوية الغير عضوية على البيئة ، وحرصا علي سلامة صحة الأنسان ونوعية مياه الشرب فقد أهتمت المواصفة القياسية لمياه الشرب رقم 458 لسنة 2007 بالمكونات العضوية حتي أشتملت علي 82 مركباً عبارة عن: مبيدات، وهيدروكربونات بترولية، وفينولات، ومذيبات هيدروكربونية وهالوجينية ومواد ناتجة عن إضافة الكلور في عمليات التعقيم. لذا فإن الطرق التقليدية أصبحت غير كافية لتقييم نوعية المياه من حيث صلاحيتها للاستخدام الآدمي. وللتاكد من جودة ونتائج التحاليل تم الأهتمام ببرنامج (Quality assurance QA and Quality control) ليقوى ويجسد فعالية بيانات التحليل، لإزالة أو تقليل الأخطاء التى ربما تتواجد فى العمليات المعملية، والتى تتسبب من الأشخاص، والأجهزة، والأدوات, وطرق أخذ العينات، وطريقة التحليل.

ومن ثم فإن الهدف الرئيس من هذه الحلقة الدراسية هو؛ تمكين كل دارس من الوقوف على اسس الطرق الحديثة في تحديد وتقدير الملوثات الغير العضوية متضمنة تطبيق برنامج (QA/QC) .
وتقييم المعمل تمهيدا لتطبيق برنامج التأمين والتحكم فى الجودة.

وبمعرفة الدارس أسس تلك النظم ومن خلال عمله وتطوير الأداء- بدءا من جمع العينات، والتأكد من دقة أداء وسائل التحليل واتباع الطرق القياسية فى التحليل مع تطبيق برامج (QA/ QC) والتى من أهدافها تقليل الأخطاء فى المعمل والتى تنعكس على دقة النتائج المتحصل عليها -سيكون هناك فى النهاية سجلات للنتائج وتحليلها يمكن الاعتماد عليها لتأكيد سلامة مياه الشرب.

وفى نهاية البرنامج نكون قد أعددنا كوادر من الكميائيين على دراية كافية بالأسس النظرية والعملية لكيفية القيام بالتحاليل الكميائية للملوثات الغير العضوية وفق برنامج التحكم فى جودة النتائج . وقادرين على نقل ما تلقوه خلال الدورة الى مجموعة أخرى من العاملين وبالتالى تتسع الخبرة النظرية والعملية ويتم تحديث خبراتهم بكل ما يخدم العاملين فى هذا المجال والذى بدوره ينعكس على نوعية المنتج من مياه الشرب.

2. المجموعة المستهدفة

- الكيميائين العاملين بالمعامل المركزية لشركات المياه التابعة للشركة القابضة لمياه الشرب والصرف الصحى.

3. عدد المتدربين

يبلغ عدد المتدربين المقدر لحضور دورة التحاليل العضوية في المياه (التحاليل الكيميائية- أسس استخدام التحاليل الكروماتوجرافية- التحكم في جودة ودقة النتائج)

- عدد 7 متدرب بالمعمل المركزي بقنا
- عدد 2 متدرب من كل معمل من المعامل المركزية بالشركات التابعة الإجمالى من 12- 15 .
- مكان الدورة: المعامل المركزية بالقاهرة ، البحيرة.

4. منهجية التدريب

تعتمد منهجية التدريب بالدورة على عدة اسس يكون الهدف الرئيسى منها توصيل المعلومة بسهولة ويسر للمتدرب وكذلك ضمان المشاركة الفعالة من المتدربين أثناء جلسات التدريب والتأكد من الفهم الكامل لمحتويات وموضوعات الدورة والتدريب العملى والشخصى على الموضوعات التى ستتناولها الدورة.
هذا ويمكن تلخيص المنهجية المتبعة فيما يلى:

- **المحاضرات:** التى يلقيها المدرب ذو الخبرة بهدف توصيل أحدث المعلومات على صورة نظرية وعملية والتأكد من التطبيق العملى بطريقة صحيحة وعلى

أساس من الفهم مما يمكنه من تلاشى الأخطاء التى من الممكن أن تلعب دورا فى صحة النتائج التى يتحصل عليها والتى تهتم بجودة مياه الشرب.

- **الشرائح Power point:** التى تعرض أثناء الشرح لإبراز النقاط الرئيسية لكل موضوع فى تسلسل منطقى ولضمان وتثبيت المعلومة لدى المتدرب.
- **المناقشات المفتوحة:** ويديرها المدرب أو المحاضر وتتيح هذة المناقشات الفرصة لتبادل الأراء وتوجبه الأسئلة و الحصول على معلومات جديدة كما إنه يتم من خلالها نقل المعارف والخبرة العملية والنظرية من المدرب إلى المتدربين وتصحيح ا لمفاهيم غير الصحيحة لدى المتدربين.
- **دراسة الحالات الواقعية:** وهى تفيد فى عرض المشاكل العملية التى يواجهها المتدربون أو التى سوف يواجهونها فى عملهم و أساليب التغلب عليها بالاسلوب العلمى الصحيح.
- **التدريب العملى:** والذى سيتاح بصورة فردية لكل متدرب باستخدام الطرق القياسية الحديثة لضمان الفهم التام والتطبيق الصحيح من المتدرب للمعلومات والطرق العملية التى تم تدريسها.
- **المراجع العلمية:** يتم إعطاء المتدرب المراجع العلمية التى أعتمد عليها والتى يمكن الرجوع إليها لزيادة التعمق فى المجال وكذلك الإشارة ومناقشة الكود الخاص بتشغيل محطات معالجة مياه الصرف والمواصفات الحديثة الحاكمة والمعمول بها فى مصر وعلى المستوى الدولى فى مجال مياه الصرف.
- **فى نهاية الدورة يتم تقييم الحاضرين من خلال اختبار تحريرى فى مواد الدورة.**

5. <u>مساعدات التدريب</u>

- جهاز عرض الشرائح (Power Point Projector)
- سبورة بيضاء أو سبورة ورقية
- شاشات عرض.

6. <u>مكان التدريب و طريقة الجلوس بجلسات التدريب</u>

يجلس المتدربون وفى مواجهتهم المحاضر فى المنتصف وعلى يمينه جهاز الكمبيوتر لعرض الشرائح Power Point وشاشة العرض وعلى يساره السبورة البيضاء أو السبورة الورقية ويكون وضع كل من شاشة العرض والسبورة بحيث يسمح بسهولة الرؤية لجميع المتدربين.

وتقدر المساحة المطلوبة لقاعة التدريب بما لا يقل عن 5 × 7 مترا لتستوعب المتدربين والمدرب لتسمح بسهولة حركة المدرب وإمكانية وصولة لأماكن جلوس المتدربين. ويلزم أن تتوفر بالقاعة الإضاءة اللازمة والتهوية الكافية والأجهزة الصوتية المناسبة.

ثانيا: خطة التدريس بالدورة التدريبية

أ. دورة التحاليل الغير العضوية في المياه

محاضر: أستاذ مساعد . منى خورشيد

تدريبات عملية: مساعد من هيئة العاملين بالمعمل الذى تتم فيه الدورة وذلك بالتناوب.

1.أهداف الدورة

الهدف الرئيس من هذه الحلقة الدراسية هو؛ تمكين كل دارس من الوقوف على اسس الطرق الحديثة في تحديد وتقدير الملوثات العضوية متضمنة تطبيق برنامج QA/QC) وتقييم المعمل تمهيدا لتطبيق برنامج التأمين والتحكم فى الجودة.

التأكد من دقة أداء وسائل التحليل واتباع الطرق القياسية فى التحليل مع تطبيق برامج QA/ QC والتى من أهدافها تقليل الأخطاء فى المعمل والتى تنعكس على دقة النتائج المتحصل عليها –سيكون هناك فى النهاية سجلات للنتائج وتحليلها يمكن الاعتماد عليها لتأكيد سلامة مياه الشرب.

وفى نهاية البرنامج نكون قد أعددنا كوادر من الكميائيين على دراية كافية بالأسس النظرية والعملية لكيفية القيام بالتحاليل الكميائية للملوثات الغير عضوية وفق برنامج التحكم فى جودة النتائج . وقادرين على نقل ما تلقوه خلال الدورة الى مجموعة أخرى من العاملين وبالتالى تتسع الخبرة النظرية والعملية ويتم تحديث خبراتهم بكل ما يخدم العاملين فى هذا المجال والذى بدوره ينعكس على نوعية المنتج من مياه الشرب.

2 موضوعات الدورة

ويشتمل البرنامج علي شرح تفصيلي ومبسط للمواضيع التالية

الملوثات الغير عضوية (المعادن الثقيلة)

ويستعرض انواع طرق التحليل المستخدمة وعملية أخد وحفظ العينات .

التحليل الكيميائي للمعادن

Analytical Procedures for Metals

ويشتمل علي كيفية المعاملة الأولية للعينات تبعا للمعادن المراد تقديرها (المعادن الذائبة– الغير ذائبة(suspended metal) – المعادن التى يمكن استخلاصها بالحامض). كما يشتمل على طرق الهضم المختلفة وكيفية إختيار الحامض.

التحقق من صحة النتائج:Quality Control:

يتضمن هذا الفصل العناصر الأساسية لبرنامج التحقق من صحة النتائج ويحتوي علي تعريف الدراس بالعناصر الأساسية لبرنامج التحكم في جودة نتائج تحليل الملوثات الغير عضوية، وكيفية القيام بالعمليات الحسابية لقياس دقة وحساسية وكفاءة الطريقة المستخدمة

أسس أستخدام جهاز الإمتصاص الذرى وجهاز ICP :

ويشتمل هذا الفصل علي اسس استخدام أجهزة القياس المختلفة (AAS and ICP) ، الأجزاء الرئيسية للجهازين طريقة تحديد وتعين الملوثات، و الظروف المختلفة التي تؤثرعلي عمليات التحليل.

3 مدة الدورة

تستغرق الدورة فى المعامل المركزية مدة ستة أيام خلال أسبوع. و يبدأ العمل يوميا من الساعة التاسعة صباحا حتى الساعة الرابعة والنصف بعد الظهر، أى مدة ثماني ساعات ونصف يوميا يتخللها أستراحتان الاولي مدتها نصف ساعة أما الثانية أستراحة مدتها ساعة لتناول المشروبات والغداء (بواقع ساعاتان نظرى وأربع ساعات عملى.)

أ.4 البرنامج الزمنى للدورة

اليوم	الجلسة	التوقيت	الموضوع	المحتوى
اليوم الأول	جلسة الإفتتاح	8:30	إستقبال و تسجيل المشاركين فى الدورة	
	الجلسة الأولى	11-9	التعارف المقدمة والهدف من الدورة واختبار تمهيدي لتحيد مستوي المتدربين	• أهداف الدورة • أهمية برنامج التحاليل المتقدمة • محتويات الدورة • تقيم مبدئي للمتدربين
	استراحه	11.30-11.00	تـــناول الشـــــــــــــاى	
	الجلسة الثانية	2.30-12.00	الملوثات الغير عضوية	• المقدمة
		2.00-1.00	تنـــاول الغـــــــــــداء	
	الجلسة الثالثه	3:00 – 2.00	تقدير المعادن الثقيلة فى عينات المياه	• انواع طرق التحليل • عملية أخد وحفظ العينات • المعاملة الأولية للعينات و طرق الهضم المختلفة.
	استراحه		عملى	• تجهيز الزجاجيات اللازمة • الكيماويات والكواشف • أجهزة وأدوات المعمل.

اليوم الثانى	**الجلسة الأولي**	11.00 -9:00	**التطبيق العملي لطرق الهضم المختلفة**	**تحليل العناصر الثقيلة متل الحديد والمنجنيز والنحاس**
	استراحه	11:30-11	**تناول الشـــــــــــــــاى**	
	الجلسة الثانية	1.00-11.30	• **شرح نظرية عمل جهاز طيف الامتصاص الذرى Flame وطرق تحضير المحاليل القياسية .**	
	استراحة	2.00-1.00	**تنـــاول الغـــــــــــداء**	
	الجلسة الثالثة	4:30 – 2:00	**عملى**	**تطبيق طرق تحضير المحاليل القياسية**
اليوم الثالث	**الجلسة الأولي**	11.00 -9:00	**شرح نظرية عمل جهاز طيف الامتصاص الذرى Graphite وطرق تحضير المحاليل القياسية .**	•
	أستراحه	11:30-11	**تناول الشـــــــــــــــاى**	
	الجلسة الثانية	1.00-11.30	**عملى**	•
	استراحة	2.00-1.00	**تنـــاول الغـــــــــــداء**	
	الجلسة الثالثة	4:30 – 2.00	**عملى**	• **تطبيق طرق تحضير المحاليل القياسية**

اليوم الرابع	**الجلسة الأولي**	11.00 – 9:00	**نظرى**	• **شرح نظريه عمل جهاز(PCI)**
	الأستراحه الأولي	11:30-11	**تناول الشـــــــــــــــاى**	
	الجلسة الثانية	1.00-11.30	**التحقق من صحه النتائج**	• **تعريفاتDefinitions** • **خطوات التحقق من صحة النتائج** • **التحقق من جودة ودقة النتائج**
	استراحة	2.00-1.00	**تنـــاول الغـــــــــــداء**	
		4:30 – 2.00	**عملى**	**قياس العناصر الثقيله مثل الزئبق على جهاز طيف الامتصاص الذرىHydride system**
اليوم الخامس	**الجلسة الأولي**	11.00 -9:00	**نظرى**	• **شرح نظريه عمل جهاز(PCI)**
	الأستراحه الأولي	11:30-11	**تناول الشـــــــــــــــاى**	
	الجلسة الثانية	1.00-11.30	**التحقق من صحه النتائج**	• **تعريفاتDefinitions** • **خطوات التحقق من صحة النتائج** • **التحقق من جودة ودقة النتائج**
	استراحه	2.00-1.00	**تنـــاول الغـــــــــــداء**	

اليوم السادس	**الجلسة الأولي**	11.00 -9:00	**مراجعة عامة**	
	استراحه	11:30-11	**تناول الشـــــــــــــــاى**	
	الجلسة الثانية	1.00-11.30	**التقيم النظري للمتدربين**	
	استراحة	2.00-1.00	**تنـــاول الغـــــــــــداء**	
	الجلسة الثالثة	4:30 – 2:00	**التقيم العملي للمتدربين**	

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الكـــيمياء الغير عضـــويه المتـقـــدمه

Advanced Inorganic Chemistry

إعداد:

أستاذ مساعد / منى خورشيد

المعمل المركزى لتحليل متبقيات المبيدات والعناصر الثقيلة فى

الأغذية- مركز البحوث الزراعية

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الملوثات الغير عضوية

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الهدف من الدورة

- الهدف الرئيس من هذه الحلقة الدراسية هو؛ تمكين كل دارس من الوقوف على اسس الطرق الحديثة في تحديد وتقدير الملوثات الغيرعضوية متضمنة تطبيق برنامج (QA/QC) .
- تقوية وتجسيد فعالية بيانات التحليل، لإزالة أو تقليل الأخطاء التى ربما تتواجد فى العمليات المعملية، والتى تتسبب من الأشخاص، والأجهزة، والأدوات, وطرق أخذ العينات، وطريقة التحليل. وتقييم المعمل تمهيدا لتطبيق برنامج التأمين والتحكم فى الجودة

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- إعداد كوادر من الكميائيين على دراية كافية بالأسس النظرية والعملية لكيفية القيام بالتحاليل الكميائية للملوثات الغيرعضوية وفق برنامج التحكم فى جودة النتائج . وقادرين على نقل ما تلقوه خلال الدورة الى مجموعة أخرى من العاملين وبالتالى تتسع الخبرة النظرية والعملية
- ويتم تحديث خبراتهم بكل ما يخدم العاملين فى هذا المجال والذى بدوره ينعكس على نوعية المنتج من مياه الشرب

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- تحديد نوعية وجودة المياة بإجراء الإختبارات لتقدير الملوثات غيرعضوية ومقارنتها بالمواصفة القياسية لمياه الشرب رقم ٤٥٨ لسنة ٢٠٠٧.

- التحقق من توافر الهدف الأساسى من وراء معالجة المياه وهو حماية الصحة العامه ومنع انتشار الأمراض بين جمهور المستهلكين

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- الوقوف على اداء كافة مراحل المعالجة ومعالجة القصور ان وجد فى احداها.

- الوقوف على حالة شبكات التوزيع والحاجة الى الصيانه من خلال تقدير مدى التغير فى خصائص المياه نتيجة مرورها فيها ولضمان وصول المياه الى المستهلك باقل تغيرات ممكنه فى الخصائص عند خروج المياه من محطة المعالجه.

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برنامج الدورة

الملوثات الغيرعضوية

- ويحتوي علي أنواع الملوثات العضوية وتقسيمهاعلي طرق استخلاص المبيدات العضوية والهيدروكربونات والمواد الفينولية، كما يتضمن الفصل كيفية تنقية وفصل مكونات العينة بإستخدام عمود الفصل والمحتوي علي مواد أدمصاص مختلفة مثل أكسيد الالمونيوم والسيلكا جل والفلوسيل.

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- كيفية تحضير المحاليل العيارية لمبيدات الهيدروكربونات الكلورية والفسفورية ومجموعة الكربامات كما يتضمن ظروف تشغيل جهاز الكروماتوجراف الغازي والسائل في تحديد وتعين المبيدات العضوية في مياه الشرب

- كيفية تحديد وتعين الملوثات العضوية الهالوجينية الناتجة من أضافة الكلور الي مياه الشرب وتفاعل الكلور مع المواد العضوية وخاصة الأولية منها مشتملا علي تحضير المحاليل القياسية وظروف تشغيل جهاز الكروماتوجراف الغازي.

- العناصر الأساسية لبرنامج التحقق من صحة النتائج ويحتوي علي تعريف الدراس بالعناصر الأساسية لبرنامج التحكم في جودة نتائج تحليل الملوثات العضوية، وكيفية القيام بالعمليات الحسابية لقياس دقة وحساسية وكفاءة الطريقة المستخدمة.
- اسس استخدام أجهزة الكروماتوجراف ، الأجزاء الرئيسية للجهازطريقة تحديد وتعين الملوثات، والظروف المختلفة التي تؤثرعلي عمليات التحليل؛ كدرجة الحرارة والوسط السائلي والغاز الخامل ونوع الكاشف

الملوثات الغير العضوية الشحيحة: Inorganic Micropollutants

مياه الشرب عرضه للتلوث بالمواد العضوية والمعادن الثقيلة نتيجة للثورة الصناعية والازدياد في استخدام المبيدات والأسمدة العضوية والمواد البتروكيميائية. بالإضافة إلى استخدام الكلور في عملية تنقية مياه الشرب ينتج عنه تكون مواد عضوية هالوجنية ذات تأثير ضار على صحة الإنسان ، مثل مشتقات الميثان وحمض الخليك الهالوجينية (Trihalomethanes and Haloacitic acids)

لذا فإن الطرق التقليدية لتحليل المياه بالرغم أهميتها أصبحت غير كافية لتقيم نوعية المياه من حيث صلاحيتها للاستخدام الأدمي. لذلك وجب دراسة الطرق الحديثة لقياس الملوثات الدقيقة (Micropoiillutants Analysis) .

- ومن هذا المنطلق وجب دراسة الطرق الحديثة لقياس العناصر المعدنية (heavy metals analysis) و تقسم العناصر المعدنية (Heavy Metals) إلى :

- عناصر معدنية كبرى (Macro : Major Elements): وتمثل ٣٥ % من وزن الجسم مثل الكالسيوم (١.٢ – ٢ %) والفسفور (٠.٠٧) والصوديوم والبوتاسيوم والكلور والكبريت والماغنسيوم.

- وعناصر معدنية صغرى ضرورية للجسم (Micro : Essential elements):

- وقد تسمى بالعناصر الدقيقة كالحديد والزنك والنحاس ولامنجنيز والكوبلت واليود والمولبيدنيم.

- أو العناصر المحتمل أنها ضرورية للجسم (Possibly Essential Elements) كرصاص والكادميوم والزرنيخ والسلينيوم والفلور والفانيوم والكروم والقصدير ولنيكل والسيليكون والبرورون والباريوم.

- كما توجد عناصر غير ضرورية للجسم ملوثة (Non Essential Elements:Contaminant) مثل الألومنيوم والأنتيمون والبزموت والجرمانيوم والذهب والفضة والربيديم وهذا يؤدى الى إصابة الانسان بالعديد من الأمراض نتيجة تلوث مياه الشرب.

تلوث المياه بالرصاص (water Lead Pollution) :

- تتلوث المياه بعنصر الرصاص نتيجة ملامسة الهواء الملوث به للمسطحات المائية أو الهواء الملوث بعادم السيارات أو مداخن مصانع الكبريت والطلاء والورق والقصدير والصفيح كما يمكن وأن تتلوث المياه نتيجة طلاء الخزانات وأنابيب المياه والجدران الداخلية أو يستخدم فى اللحام والذى يتحول لكربونات رصاص لا تنحل فى الماء فيعق تسرب الرصاص من جديد للماء وتزداد نسبة الرصاص فى الليل والصباح الباكر لركوده المياه به. أو قد يكون مصدر التلوث هو سحب ملوثة به وممطرة وقد يكون مصدر التلوث هو صرف مياه مخلفات المصانع بالأنهار والبحار القريبةمن هذه المصانع.

- وتبلغ نسبة الرصاص بالمياه ١-١٠ ميكروجرام/لتر (١-١٠.٠ جزء فى البليون :ppb).

ولوحظت زيادة فى تركيز الرصاص بشكل عالى مخيف فى الآونة الأخيرة فى مياه المحيطات فتضاعفت خمس مرات خاصة فى شمال المحيط الأطلنطى وكذلك بلغ عدة أجزاء فلا المليون على المياه الإقليمية لشواطئ لبنان (أى على بعد يبلغ ٢٢٠ متر من الشواطئ) فى حين بلغت مستوى هائل ومخيف للغاية (١٥٠ – ٤٨٠ جزء فى المليون) بأنسجةالكائنات البحرية فى خليج تسالونيك خاصة بالقرب من معمل إنتاج مركب تترا إيثيل الرصاص.

- وتراكم جزيئات الرصاص بأنسجة الكائنات الحية كالطحالب والقشريات ومن كلاهما ينتقل عبر السلاسل الغذائية الحيوانية ويصل فى النهاية للانسان

ارتفاع نسبة الرصاص عن ٠.١ ملجم/ لتر (٠.١ جزء فى المليون) بمياه الشرب يؤدى لظهور أعراض التسمم بالرصاص فى صورة خطوط زرقاء مسودة باللثة وتكسير كرات الدم الحمراء وإمساك انخفاض نسبة الهيموجلبين مع ألم بالصرة أو تحتها وبزيادة شدة الأعراض تؤدى لإضطرابات عصبية تصل للشلل الطرفى والصرع والتشنجات ثم غيبوبة (comma). كما أنه يعوق إفراز حمض اليوريك مما يؤدى لظهور أعراض مرض النقرس.

وتحتوى المياه السطحية على مستوى من الرصاص يبلغ ١٠ ميكروجرام / لتر ١٠ جزء فى البليون : ٠.٠١٠ جزء فى المليون / لتر) ويجب عدم استخدام مياه الشرب التى تصل فيها تركيز الرصاص إلى ٥٠ ميكروجرام/لتر (٠.٠٥٠ جزء فى المليون) حيث يترسب فى الأنسجة العظمية والكبد والكليتين فى فى صورة ثالث فوسفات الرصاص يتراكم بالعظام مع فترات التعرض الطويلة ويحل محل الكالسيوم كما يتراكم بأنسجة المخ فيتلفها مما يؤدى للصرع بوصول تركيزه إلى ١٠٠ ميكروجرام/ لتر (٠.١ جزء فى المليون) يصبح الماء السام).

- ولذا يجب استخدام مياه الصنبور العادى بالمنزل ترك المياه تتدفق بدون استخدام لعدة ثوانى دون استخدامها حيث يتسنى التخلص من نسبة عالية من الرصاص بها.

- ويوجد الرصاص بكميات ضئيلة بالجسم حيث يدخل عن طريق الفم عند الشرب للمياه الملوثة به حيث تفرز نسبة منه بالبراز وأخرى بالبول عن طريق الكليتين ونسبة ثالثة تمتص وتصل حتى ٢٠% وتتحرك لكبد الذى بدورة يحركها مع العصارة الصفراء للأمعاء (فى حين يدخل الرصاص مع الهواء الملوث المستنشق خلال الشعب الهوائية للدم ولا يمر عن طريق الكبد) ، ونظراً لتشابه عمليتى تمثيل الرصاص والكالسيوم فى الجسم فأن العوامل المحفزة لتخزين الكالسيوم بالجسم تكون هى نفسها العوامل المحفزة لتخزين الرصاص.

- ويؤدى التسمم المزمن بعنصر الرصاص إلى تبلد فكرى وتخلف عقلى وعدم المقدرة على التركيز مع ضعف فى الذاكرة وصمم وفقدان النطق أو العمى ثم الشلل لليد اليمنى ثم اليسرى وأخيراً شلل المخ وفشل كلوى.
- أما بالنسبة للأطفال فزيادة نسبة الرصاص يأجسادمهم تؤدى لانخفاض مستوى الذكاء بوضوح (وذلك لزيادة نشاطهم مع قلة محتوى أجسامهم النسبى من الدم).

- ويلاحظ أن وجود الرصاص بدم الأم الحامل (٨ ميكروجرام/١٠٠ ملل دم) يؤدى لولادة أطفال يحتوى دمهم على نسبة كبيرة من الرصاص وقد يصل إلى ٢٥ ميكروجرام/١٠٠ ملل دم كما يؤدى الرصاص بدم الأم إلى ولادة أطفال ذات أوزان أقل من المتوسط بحوالى ٢٠٠ جم وضعاف لإستجابة المؤثرات البصرية والسمعية لحوث إعاقة فى نمو خلايا المخ.

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▪ تلوث المياه بالزئبق (water Mercury Pollution)

تعد ملوثات الزئبق العضوية أشد خطراً وسمية على الصحة العامة عن مركبات الزئبق الغير عضوية والتى يمكن لجسم الانسان إفرازها بالبول (مثل الزئبق – فينيل خلات الزئبق – داى ميثيل الزئبق).

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ويكمن سبب خطورتها وسميتها العالية فى درجة ثباتها العالية (High stability) وتراكمها الحيوى (Bio accumulation) داخل أنسجة الجسم خاصة بأنسجة المخ فتسبب شلل وتشوهات (Teratogenic) وضعف بالبصر والسمع علاوة على كونها مواد مطفرة (Mutagenic) فكلما زادت درجة صعوبة تحللها كلما زادت درجة خطورتها كما تتراكم بأنسجة السمك الموجودة فى مياه ملوثة يصل تركيزها بها ٠.١ ميكروجرام/لتر (٠.٠٠٠١ جزء فى المليون)

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- وعند بلوغ مستوى تركيزه فى مياه الشرب سامة حيث أن أقصى حد مسموح بتواجد فى الماء (MACw) هو ٠.٥ جزء فى المليون وتزداد خطورة الزئبق اللاعضوى بتحوله لمركبات زئبق عضوية سامة كمثيل الزئبق للكائنات الحية الدقيقة حيث أن المركبات الزئبقية العضوية أشد سمية وخطراً على الإنسان فهى تمتص وتتراكم فى حين أن المركبات الزئبق العضوية يتم إخراجها عن طريق البول.

Seite 27

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- كذلك أظهرت التقارير عن تحليل عينات بروتين سمكة تم صيدها من بحيرة سانت كلير بكندا احتواءها على الزئبق فى صورة ثنائى فينيل الزئبق يرتبط بالبروتين عن طريق ذرة الكبريت كذلك كان الحال فى بحيرة ليمان بسويسرا خاصة فحالة العوالق (الهائمات) النباتية والجسيمات والتى أعزيت لصرف مياه المصانع فى مياه نهر الرون الذى تصل مياهه للبحيرة.

Seite 28

- ويلاحظ أن تركيزه يزداد تركزاً بارتقاء كائنات السلاسل الغذائية فهو بالإنسان > الطيور > الأسماك > القشريات > النباتات > الهائمات ويعزى ذلك لزيادة معدل تراكمه الحيوى على هذا النحو وهو ما يسمى بالتضخم الحيوى (Bio magnification)

- كما ظهر أثره الواضح فى التراكم الحيوى والتضخم بوضوح فى مرض الميناماتا والذى ترجع تسميته إلى خليج ميناماتا فى اليابان حيث أدى صرف أحدى مصانع البلاستيك لمخلفاته فى مياه الخليج وكانت محتوية على ٥٠١ جزء فى المليون زئبق مما أدى لتسمم الأسماك والصيادين وظهرت الأعراض فى صورة لعثمة فى النطق وزغلله وشلل بالأطراف لتدمير الخلايا العصبية فى المخيخ والمخ الأوسط كما أدى لحدوث بعض حالات تغير جينية

- كما أدت إلقاء فضلات مصانع الزئبق لزيادة نسبة وفيات سكان نهر دامسى فى واشنطن أونهر هومسون فى نيويورك وبحيرة توركش بولاية ميتشجان ولهذا قامت سلطات هذه الولايات الثلاثة بحظر السباحة أو تناول المياه أو الأسماك من هذه المصادر الثلاثة.

ولقد بلغت نسبة الزئبق بالسواحل العربية على البحر الأبيض المتوسط ١ مليجرام / كم سمك وهو ما يشير بأنه عند استهلاك ٢ كم سمك أسيوى يؤدى بدور لامتصاص ما يوازى ٢ملليجرام يثبت منها ٨٠ ميكروجرام بالجسم / أسبوع وعليه تظهر أعراضه (تأثيراته) الأولى بعد ٧ سنوات وتحدث الوفاة بعد ٢٠ عام ومما يجدر بالذكر فى هذا الصدد وهو ما أثار الدهشة تواجد تركيزات ملحوظة من الزئبق فى الحيوانات القطبية كالدب القطبى والطيور كالبنجوين رغم رغم بعدها عن مصادر التلوث به وقد أعزى ذلك إلى حدوث تلوث بإحدى مراحل السلسلة الغذائية حيث انتقلت متبقيات الزئبق لها خاصة الأسماك

- وتقوم الكائنات الحية الدقيقة الغير هوائية مثل بكتيريا C losrtidum Cocheaealcor والتى يكثر وجودها فى الترسبات المائية بتحويلها لمثيل الزئبق أو داى ميثيل الزئبق وهو أشد سمية.

- **تلوث المياه بالكادميوم (Water Cadmium Pollution)**

يتم تلوث المياه بعنصر الكادميوم نتيجة إلقاء مخلفات المصانع والتى تصل إلى ١٠٠٠ طن سنوياً من معدن الكادميوم فى المسطحات المائية خاصة مخلفات مصانع المواسير والطلاء أو لمرور مياه بمواسير بلاستيك يدخل فى تركيبها. والكادميوم ملوث خطر جداً لتراكمه بأجسام الكائنات الحية النباتية والحيوانية خاصة المائية منها كالسمك والقشريات وأخيراً يصل الانسان بقمة السلسلة الغذائية (Food chain).

- ويجب ألا يزيد مستوى تواجده بالمياه عن ١٢٠ ميكروجرام / لتر (١٢%جزء فى المليون) وزيادة مستواه عن ذلك تجعل المياه غير صالحة للاستخدام الآدمى وهنا يجب الأخذ فى الاعتبار أن مواسير المياه البلاستيكية الصنع تؤدى إلى تسرب الكادميوم من مادتها للمياه المارة فيها وعند بلوغ مستواه بالمياه إلى ٢٠٠ ميكروجرام / لتر (٠.٢ جزء فى المليون) وتصبح المياه مميتة.

- حيث يؤدى الكادميوم إلى اضطراب فى النمو العام مع تغيير فى تركيب الدم وفقر الدم (أنيميا) وظهور مرض (أيتاى – أيتاى) كذلك حدث تسرب للكادميوم من نفايات إحدى المصانع المطلة على نهر بالبرازيل للحالات تسمم فى صورة اضطرابات عصبية وارتفاع فى ضغط الدم حيث بلغت نسبته بأجسام أسماك مياه النهر إلى ٢١ مللجرام / كجم سمك.

٤- تلوث المياه بعنصر الزرنيخ (Water arsinous pollution) :

يحدث تلوث المياه بعنصر الزرنيخ من عدة مصادر أكثرها التعرض لبقايا السموم الزرنيخية المستخدمة فى مكافحة الآفات الحشرية والحيوانية والحشائش سواء لأنجرافه فى الهواء (Drift) أثناء الرش أو أثناء التعفير وسقوطها على الأسطح المائية المحيطة أو المترسبة منها على الأسطح المعاملة والتربة والحادث لها عملية سريان (Dripping : Run off) أو الغسيل (Washing) ثم تتخلل حبيبات التربة وتتشرب (Leashing) حتى تصل إلى المياه الجوفية وكذلك مياه صرف المصانع والقائمة بطحن وتجهيز مستحضراته.

- ويلاحظ أن مركبات الزرنيخ الثلاثية أشد فى درجة سميتها عن الخماسية (Penta vallant) لارتفاع معدل ذوبان الأولى كثيراً فى الماء (حيث لمعدل الذوبان وكذلك درجة نعومة المادة أثرهما الفعال فى ارتفاع السمية فكلما زادت درجة النعومة كلما زاد معدل التخلل والامتصاص
- كذلك فكلما زادت نسبة الذوبان زادت نسبة انفراد الزرنيخ الذائب فى الماء) (حيث تؤدى ارتفاع درجة الحرارة أو الرطوبة النسبية أو الندى أو زيادة نسبة ثانى أكسيد الكربون بالجو كذلك المناطق الساحلية حيث زيادة مستوى كلوريد الصوديوم بالجو إلى زيادة انفراد الزرنيخ الذائب)

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- والتالى تزداد درجة السمية والضرر الجانبى على النباتات والحيوانات وبامتصاصها بالجسم خلال الجلد أو بوصولها للقناة الهضمية عن طريق شرب مياه ملوثة بها أو أطعمة تحتوى على مخلفاتها تبدأ أعراض التسمم المعدى فى صورة آلام شديدة بالمعدة ثم اسهال وتبول مدمم وشحوب وبرودة بالجسم مع العطش ونقص التنفس ثم يدخل فى الغيبوبة فالوفاة ، حيث تبلغ الجرعة القاتلة ٥ – ١٠٠ ملليجرام / كج من وزن الجسم تبعاً لنوع الكائن المعامل ونوع المركب الزرنيخى.

Seite 39

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وبوصولها للجسم ترتبط بذرات كبرت المستقبلات الحيوية (Bio receports) خاصة الإنزيمات المحتوية على مجاميع سلفهيدريل (-SH) فتثبطها مثل إنزيم لاكتيك ديهيدروجينيز وألفا جلسرو فوسفات ديهيدروجينيز والسيتوكروم أكسيديز فهى تستهدف روابط الكبريت وتكوين مركبات كبريتية فتختفى مجاميع السلفهيدريل الحرة والتى تقوم بدور كبير فى المحافظة على على الشكل المميز للبروتين لذا فالحقن بالجلوتاثيون أو البال (PAL) يمنع استمرار التسمم لتنافس مجاميع السلفهيدريل على جزئيات الزرنيخ وترتبط به وتبعده عن الأنسجة بما يؤدى لعمليات ترسب : تجلط (Coagulation) خاصة عند ارتفاع تركيزه فجزيئات المركبات الزرنيخية تستهدف فى المقام الأول روابط الكبريت والتى لها دورها الهام فى حفظ الشكل البنائى المميز (Configuration) لجزئيى البروتين.

Seite 40

كما ترتبط مع المرافق الأنزيمى (أ) الأنزيمات التى تقوم بنزع الهيدروجين من المركبات الحيوية أو ترتبط بالمواد المؤكسدة فتمنع عملية الفسفرة التأكسيدية لجزيئات الأدينوسين داى فوسفات (ADP) وتكوين الناتج المفسفر (ATP).

- ويلاحظ إمكانية تخلص الجسم من التركيزات المنخفضة بواسطة الكلية وإخراجها عن طريق المسار البولى وفى بعض الأحيان يفرز فى البراز حيث ظهر فى الأبقار لمدة تصل إلى ١٤ يوم بينما وصلت فى البراز حتى ٧٠ يوم وهنا يجب الأخذ فى الاعتبار فى هذا الصدد بأن التركيزات الضعيفة منه تعد منشطة للجسم وفاتحة للسهية (أكلة الزرنيخ)

أما فى تايوان فينتشر مرض القدم السوداء (Black foot) لارتفاع مستوى الزرنيخ فى مياه الشرب الجوفية كذلك وجدت تركيزات عالية منه فى مياه شرب بقرية توربوان بالمكسيك (٤-٦ جزء فى المليون).

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- أما عند التعرض لجرعات عالية عن الحد الذى يمكن عنده أن يتخلص الجسم منها فإن الزائد منها يتجمع بالدرجة الأولى بالكبد فيسبب تدهن الكبد (Fatty Liver) ثم الكلية ثم بعض الأنسجة الأخرى كالعظام والجلد والأظافر والشعر.

Seite 43

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- أما بالنسبة لتأثيرات مركبات الزرنيخ السامة على النباتات التى يتخللها سواء عن طريق المواضع الرقيقة فى كيوتيل الأوراق بالمجموع الخضرى حيث يبقى بها ولا يتحرك. ويلاحظ أن درجة التخلل تزداد بارتفاع الرطوبة أو عن طريق الجذور فترتفع فيها لأعلى بالمجموع الخضرى وهنا يؤثر كسم بروتوبلازمى (Protoplasmic poisons) فتسود الأوراق وتموت (حروق موضعية). وتحدث عقب عملية إمتصاصه خلال المجموع الخضرى زيادة سرعة التنفس وهنا تتحول الأوراق للون الأصفر ثم تسقط.

Seite 44

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٤- تلوث المياه بالنحاس Water Copper pollution:

يدخل النحاس الجسم عن طريق المياه والأغذية الملوثة أو الهواء الملوث ثم يمتص بالأمعاء معتمداً على البروتين المرتبط (Metallothionine) بآلية غير واضحة للآن وله فى ذلك علاقة بالزنك والكادميوم وسرعان ما يرتبط بألفا-جلوبين : سيرولوبلازمين (Ceroloplasmine) ويخزن بالكبد كبروتين يسمى (Hepatocupreina) حيث يطلق على هذا البروتين بروتين كرات الدم الحمراء (Cerebrocuprin) خلايا الأعصاب اسم مشترك هو (Cytocuprin).

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- يطرح النحاس خارج الجسم عن طريق البراز مع إفرازات الصفراء أو يخرج فى البول (٤%).

- ويدخل فى عمل أنزيم السيتوكروم أكسيديز (Cytochrome Oxidase) والأسكوربيك أكسيديز (Scorpic Oxidase) والتايروسينتيز (Tayro synthetase) واليويكيز (Uricase) وضورى لتمثيل الطاقة وتكوين الهيموجلوبين. كذلك فوجوده يحسن من امتصاص الحديد من خلايا جدر الأمعاء وتحركه بين الكبد للبلازما لبناء الهيموجلوبين كما يدخل فى تكوين العظام والميلين بالمخ ولذا فنقصه (Hypocupremia) تؤدى لمرض الكلى والتخلج (Neonatal Ataxia) والسقوط (Falling disease) لضمور وتليف عضلة القلب ونقص الإخصاب وموت الجنين وضعف التنفس وتشوه الأجنة.

Seite 47

- أما زيادة مستواه بالدم والأنسجة خاصة أنسجة الكبد فيؤدى لمرض ويلسون (Wilson) لحدوث تغيرات بنسيج المخ والكبد فيتراكم بالكبد وقرنية العين والكلى والمخ ويعالج بالمواد المستحلبة (Penicillamine) والزنك الذى يزيد إفرازه خارج الجسم والتسمم الحاد بالنحاس نادر ما يحدث يتطلب ذلك جرعة تبلغ ٢٠ مللج / كجم.

Seite 48

- وتؤدى زيادة مستوى المولبدينم (Molybdenum) بالجسم لزيادة فقد النحاس بالبول إلا أنه يقى الأسنان من التسوس ربما لأثره فى الاحتفاظ بالفلور بالجسم ويلاحظ أيضا ارتباط الأعراض معاً فزيادة بالجسم تؤدى للتسمم وظهور مرض (Peat scours) والمعالج بإعطاء مركبات محتوية على النحاس لتضاد فعلها أما نقص المولبدينم فيؤدى لإسهال ونقص النمو وفقد الدم وتأخر نضج كرات الدم.

٥- تلوث المياه بعنصر الحديد Water Iron Pollution

حيث يكون صورته بالماء على هيئة ملح ذائب هو بيكربونات الحديد التى بتعرضه للهواء الجوى يتحول للون الأحمر فالبنى. وتلوث المياه بالحديد لا يغير من طعمها ولكن زيادة مستواه عن ٠.٣ ملجم / لتر يؤدى لعسر فى الهضم وإمساك. وتحتوى بعض مصادر المياه الجوفية على تركيزات تصل ٥-٧ ملجم / لتر.

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تقدير المعادن الثقيلة فى عينات المياه

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أنواع طرق التحليل المستخدمة:

- هناك طرق عديدة تستخدم لتقدير المعادن فى عينات المياه.
- يتم أختيار الطريقة تبعا للحساسية والدقة المطلوبة فهناك طرق التحليل اللونية وهناك طرق بإستخدام الأجهزة.
- Flame atomic absorption methods concentration is (0.1 to 10 mg/L)
- Electrothermal methods

- Inductively coupled plasma emission techniques (حد التقدير أقل من ٠.٠١ ميكروجرام لكل لتر)
- Flame Photometry يعطى حساسية افضل لقياس التركيزات العالية لعناصر المجموعة الأولى والثانية.
- Anodic stripping
- Colorimetric methods

تعريف المصطلحات Definition of terms

- **العناصر الذائبة Dissolved metals**

العناصر الذائبة فى العينة الغير معاملة بالحامض والتى يمكن ان تمر خلال غساء ترشيح ٤٥ميكروميتر

- **العناصرالمعلقة Suspended metals**

يقصد بها العناصر المعلقة فى العينة الغير معاملة بالحامض ولا تمر خلال غساءالترشيح بينما تحجز على الغشاء(٤٥ميكروميتر).

- **المعادن الكلية Total metals**

يقصد بها تركيز المعادن الموجودة فى العينة بعد عملية الهضم أو مجموع تركيزات المعادن الذائبة والمعلقة ويتم تقديرها

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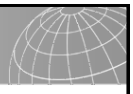

• **العناصر التى يمكن استخلاصها بالحامض Acid- extractable metals**

تركيز المعادن فى العينة بعد معالجتها بمحلول الحمض الساخن

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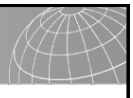

عملية أخذ وحفظ العينات
Sampling and Sample preservation

• **تتوقف العملية على نوعية الجزء المراد تحليلة والذى بدورة يحدد إذا كان سوف يتم معالجة العينات بالحامض وترشح أم تهضم.**

الاوعية المستخدم: Sample containers

- تفضل الاوعية المصنوعة من الكوارتز أو مادة TEF وكذلك يمكن أستخدام الاوعية البلاستيكية المصنوعة من polypropylene or linear polyethyleneمادة البولى بروبيلين أو البولى إثيلين بأغطية مصنوعة من مادة البولى إثيلين (polyethylene cap)
- كما يمكن إستخدام الاوعية الزجاجية المصنوعة من البوروسليكات borosilicate glass containers
- يحذر من إستخدام soft glass لإحتوائة على شوائب معدنية بتركيزات (ug/L)
- يراعى شطف الاوعية المستخدمة وكذلك ورق الترشيح بالحامض.

عملية حفظ العينات Sample preservation

- يتم حفظ العينات بعد أخذها مباشرة وذلك بإضافة كمية من حمض النيتريك المركز.
- الى أن يصبح الوسط الحامضى أقل من ٢.
- لتقدير العناصر الذائبة : يتم ترشيح العينة قبل عملية الحفظ وعادة يتم إضافة
- ml of HNO3/L sample) or (3 ml 1 + HNO3 /L sample)١.٥)
- وهذة الكمية تكون كافية لحفظ العينة لفترة قصيرة.

- يجب إستخدام حامض مركز ذو درجة نقاوة عالية .
- يتم حفظ العينات عند درجة حرارة ٤ درجة مئوية بالثلاجة لمنع التغير فى الحجم
- يمكن الإحتفاظ بالعينة لمدة ٦ أشهر -For mg/kg levels
- ماعدا فى حالة الزئبق فيمكن حفظها لمدة ٥ أسابيع
- فيجب تحليل العينة فى الحال (For ug/kg levels).

- **كيفية حفظ العينة لتقدير عنصر الزئبق:**
- تحفظ العينة بإضافة (٢ ml of 20% K2Cr2O7 / L of sample) (محضرة فى ١+١ حمض النيتريك):

- **إحتياطات عامة :**

مصادر تلوث العينات :

الأوعية المستخدمة لحفظ العينات – الأغشية المستخدمة فى الترشيح _ أغطية الأنابيب البلاستيكية ربما تكون مصدر للتلوث ببعض المعادن مثال (Cd, Zn)

كيفية اتخلص من الملوثات: وذلك من خلال إستخدام أدوات نظيفة:

الطريقة المتبعة لغسيل الأدوات:

- يتم غسيل الأدوات بمحلول غسيل خالى من المعادن
- ثم يتم الشطف بالماء وينقع فى الحامض
- ثم يتم الشطف بالماء المقطر

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- **طريقة غسيل الأدوات الزجاجية المصنوعة من الكوراتز او TEF glass materials**

Use (1+ 1 HNO3) ,(1+1 HCl)or aqua regia(3 parts conc. HCl + 3 conc. HNO3)

طريقة غسيل الأدوات البلاستيكية:

Use 1+1 HNO3 or 1+1 HCl

يتم نقع الأدوات لمدة ٢٤ ساعة عند ٧٠ درجة مئوية.

ملحوظة:

- **للتخلص من الرواسب العضوية يتم نقع الأدوات فى حمض الكروميك مع مراعاة عدم إستخدام حمض الكروميك مع الأدوات البلاستيكية.**
- **يتم إستخدام ماء منزوعة الأيونات .**

Seite 61

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التحليل الكيميائى للمعادن Analytical Procedures for metals analysis

ا) المعاملة الاولية للعينات Preliminary treatment of samples

- **يتم معاملة العينات التى تحتوى على جزيئات او مواد عضوية الى معاملة اولية قبل اجراء عملية التحليل الأسبكتروسكوبى spectroscopic analysis لتحليل مجموع المعادن (تشمل المعادن العضوية والمعادن الغير عضوية الذائبة والغير ذائبة).**
- **يتم قياس العينات عديمة اللون والواضحة (مياة الشرب) مباشرة بدون هضم العينة لتقدير مجموع المعادن بدون هضم العينة.**
- **عند تجميع العينات يتم اضافة (1.5 ml HNO3/1 L) حتى يصبح الوسط الحامضى اقل من ٢ وحينئذ يتم تحليل العينة مباشرة.**

Seite 62

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- **لتقدير المعادن الذائبة (dissolved metals):**

يتم ترشيح العينة ثم يضاف الحمض الى الراشح ويتم حفظة بالثلاجة الى ان يتم تحليلة.

- **لتقدير المعادن الغير ذائبة (suspended metals) :**

يتم ترشيح العينة ثم يتم هضم ورقة الترشيح والمادة العالقة بها.

- **لتقدير المعادن التى يمكن استخلاصها بالحمض (acid- extractable metals):**

يتم استخلاص المعادن يتم تحليل الراشح.

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معا ملة المعادن التى يمكن استخلاصها بالحامض

Treatment for acid – extractable metals

- **تحضير العينة :**
  - ينقل ١٠٠ ميللى من العينة الى كأس أو دورق ثم يضاف ٥ ميللى ١+ ١ من حمض الهيدروكلوريك المركز عالى النقاوة.
  - يتم التسخين لمدة ١٥ دقيقة فى حمام مائى.
  - يرشح المحلول بواسطة عشاء ترشيح (٤٥ µm).
  - يتم نقل الراشح الى دورق معيارى اخر ثم يكمل الحجم الى ١٠٠ ميللى بالمء الخالى من المعادن.

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ملحوظة:

اذا كان حجم العينة أكبر من ١٠٠ ميللى فانة يتم تقدير الحجم الى اقرب ٠.١ ml / weight ثم يتم تحليل العينة ويتم تصحيح قياس التركيز النهائى بالضرب فى معامل التخفيف (الحجم النهائى \ ١٠٠).

Seite 65

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▪ هضم المعادن Digestion of metals

يجب اختيار طريقة هضم مناسبة للتقليل من التداخل (interferences) الناتج من وجود المواد العضوية ولتحويل المعادن المرتبطة بالجزيئات لتكوين شكلا من اشكال المعدن (عادة المعدن الحر free metal) التى يمكن قياسها بجهاز الامتصاص الذرى او جهاز ICP..

Seite 66

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▪إختيار الأحماض Selection of acids :

يستخدم حامض النيتريك فى هضم معظم العينات وذلك لكون النيترات matrix ملائم للحقن على أجهزة الامتصاص الذرى و اجهزة ICP – MS.

تحتاج بعض العينات الى إضافة احماض أخرى لإتمام عملية الهضم مثل احماض (H2SO4- HCl- HF- HClO4) ولكن تلك الأحماض ربما تحدث تداخلات interferences عند تحليل بعض العناصر حيث انها تعد ((poorer matrix للتحليل على أجهزة الامتصاص الذرى و اجهزة ICP – MS.

Seite 67

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يستخدم حمض النيتريك عادة بمفردة فى عملية الهضم لهضم العينات سهلة الأكسدة او يتم إضافة حمض الكبريتيك او حمض الهيدروكلوريك الى حمض النيتريك عند هضم المواد العضوية القابلة للأكسدة readily oxidizable organic matter و بينما يتم اضافة حامض البيركلوريك أو الهيدروفلوريك الى حمض النيتريك عند هضم المواد العضوية صعبة الأكسدة او المعادن التى تحتوى على سليكات.

Seite 68

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Digestion procedures طرق الهضم

- الهضم بإستخدام المسطح الساخن Hot plate techniques
- الهضم بإستخدام الميكروويف (Closed vessel procedure)
- اذا كان الحجم الموصى بأخذة من العينة أكبر من سعة الدورق المستخدم فى هضم العينة فيجب تبخير العيتة .
- إذا تم تركيز العينة اثناء عملية الهضم (أكبر من ١٠٠ ميللى) فإنة يتم تقدير معدل الإسترجاع لكل matix يتم هضمة وذلك للتحقق من صحة الطريقة.

ملحوظة :

كلما إزداد حجم العينة كلما إزداد ت كمية الحمض المستخدم مما يؤدى الى زيادة الشوائب impurities

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Estimated metal concentration (mg/L) تركيز العنصر	Sample volume (ml) *حجم العينة
< 0.1	1000
0.1- 10	100
10- 1000	10

For flame atomic absorption spectrometry

A* B/C =(تركيز العنصر) metal concentration

A= concentration of metal in digested soln (mg/kg)

تركيز العينة فى المحلول المهضوم

B = final volume of digested solution, ml,and

C= sample size, ml حجم العينة

الهضم بإستخدام حامض النيتريك Nitric acid digestion:

Digestion for flame atomic absorption and high – level concentrations

التقدير بإستخدام جهاز الأمتصاص الذرى المزود بوحدة اللهب لتقدير التركيزات العالية

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الأجهزة المستخدمة: Apparatus

- مسطح ساخن Hot plate
- دورق مخروطى سعة ١٢٥ ميللى أو كاس جريفين سعة ١٥٠ ميللى

conical flasks (Erelenmeyer) 125 ml or Griffin beakers 150 ml

- يتم غسلها بالحامض ثم تشطف بالماء المنزوعة الأيونات
- دورق معيارى سعة ١٠٠ ميللى.
- زجاجات ساعة watch glasses, ribbed and unrobed

الكواشف Reagent :

حامض النيتريك المركز ذو درجة نقاوة عالية (analytical grade or trace metals grade)

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الطريقة:

- ينقل ١٠٠ مللى من العينة (المعاملة بالحامض) الى قارورة او كأس ثم يضاف ٥ ميللى من حامض النيتريك المركز.
- يتم وضع رقائق الغليان او خرز زجاجى ليساعد على الغليان وتضبط درجة الحرارة.
- يتم تبخير العينة الى اقل حجم ممكن (الى حوالى من ١٠ الى ٢٠ مللى) .

الطريقة:

- يمكن إضافة كمية أخرى من حامض النيتريك المركز لاتمام هضم العينة الى ان يصبح محلول العينة فاتح اللون وشفاف.
- يتم شطف جدران الدورق وزجاجة الساعة بالماء المقطر وترشح العينة إذا لزم ذلك.
- ينقل الراشح الى دورق معيارى سعة ١٠٠ مللى على مرتين ب ٥ مللى من الماء المقطر.
- يترك المحلول ليبرد ثم يكمل الحجم الى العلامة ويمزج جيدا

2. Determination for trace – level (<0.1 mg/l) concentrations for ICP and ICP-MS

الأجهزة المستخدمة : Apparatus

سخان كهربى مزود بوحدة تحكم فى درجة الحرارة Block heater, dry, with temperature control

انابيب من البولى بروبيلين مدرجة (تغسل بالحامض ثم تشطف بالماء المقطر)

Polypropylene tubes, graduated, rounded, round- bottom tubes with caps 17x100 mm.

Pipetters, assorted sizes or adjustable

Pipette tips

جهاز الطرد المركزى Centrifuge

الكواشف : Reagent

حامض النيتريك (double distilled).

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الطريقة:

- تنقع الأنابيب فى محلول عيارى ٢ N HNO3 ليلا أو لعدة أيام.
- ثم تشطف بالماء المقطر و يفضل ان تترك لتجف ثم تحفظ فى اكياس بلاستيكية.
- ينقل ١٠ مللى من العينة الى الانبوبة ويضاف ٥ ml of HNO3 او ١ 1 + 1 ml (ml HNO3)
- الى كلا من العينات والبلاك و المحاليل القياسية وكذلك عينات مراقبة الجودة.

Seite 77

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- يتم وضع الأنابيب فى السخان block heater وتضبط درجة الحرارة عند درجة حرارة ١٠٥° م مع وضع السدادات مع عدم إحكام الغلق .
- يتم هضم العينات لمدة ساعتين.
- يمكن إضافة كمية أخرى من حامض النيتريك المركز لاتمام هضم العينة الى ان يصبح محلول العينة فاتح اللون وشفاف.
- يترك الانابيب لتبرد ثم يكمل الحجم الى العلامة ويمزج جيدا.

Seite 78

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ملحوظة:

- إذا كانت الأنابيب تحتوى على جزئيات فإنة يستخدم جهاز الطرد المركزى لفصل الرواسب ويتم نقل الراشح الى انبوبة أخرى.

- يجب إحكام السدادة ويتم حفظها عند درجة حرارة ٤ درجة مئوية الى ان يتم تحليل العينة.

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Nitric acid hydrochloric acid digestion

الهضم بإستخدام حامض النيتريك – حامض الهيدروكلوريك

الأجهزة المستخدمة : Apparatus:

- حمام مائى

الكواشف : Reagent

- حامض النيتريك المركز ذو درجة نقاوة عالية.
- حامض الهيدروكلوريك (١+١).
- حامض النيتريك(١+١).

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الطريقة:

ا) حمض النيتريك- حمض الهيدروكلوريك

A) Total HNO3/ HCl

- ينقل ١٠٠ مللى من العينة (المعاملة بالحامض) الى قارورة او كأس ثم يضاف ٣ مللى من حامض النيتريك المركز وتغطى بزجاجة الساعة.
- يوضع الدورق على المسطح الساخن ويتم تبخير العينة الى اقل من ٥ مللى
- تبرد العينة وتشطف جدران الدورق وزجاجة الساعة بأقل كمية من الماء المقطر ثم يضاف ٥ ميللى من حمض النيتريك المركز ثم يغطى الدورق بزجاجة الساعة وينقل نرة أخرى الى المسطح الساخن و ترفع درجة الحرارة.

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- تستمر عملية التسخين ويمكن إضافة كمية من الحامض لإتمام عملية الهضم.
- يتم إضافة ١٠ ميللى من ١+ ١(HCl) و١٥ ميللى من الماء المقطر لكل ١٠٠ ميللى من الحجم النهائى المتوقع.
- وتستمر عملية التسخين ل ١٥ دقيقة أخرى لإذابة اى رواسب .
- يرشح المحلول و ينقل الراشح الى دورق معيارى سعة ١٠٠ ميللى و يكمل الى العلامة بالماء المقطر.

B) Recoverable HNO3/ HCl:

ينقل ١٠٠ ميللى من العينة (المعاملة بالحامض) الى قارورة او كأس. ٢ ml of (1+1 HNO3) و ١٠ ml of (1+1 HCl) وتغطى بزجاجة الساعة.

يتم التسخين بواسطة المسطح الساخن او بالحمام المائى حتى يختزل حجم العينة الى ٢٥ مللى .

تنقل العينة كميا الى دورق معيارى ثم يكمل الحجم الى العلامة ويمزج جيدا.

ج) طريقة الهضم بإستخدام حمض النيتريك – حمض الكبريتيك Nitric acid – Sulfuric acid digestion

الطريقة:

- ينقل ١٠٠ ميللى من العينة (المعاملة بالحامض) الى قارورة او كأس ثم يضاف ٥ ميللى من حامض النيتريك المركز وتغطى بزجاجة الساعة.
- يوضع الدورق على المسطح الساخن ويتم تبخير العينة الى ١٥ميللى ـ ٢٠ ميللى ثم تترك لتبرد.
- ثم يضاف ٥ ميللى من حامض النيتريك المركز و ١٠ ميللى من حامض الكبريتيك المركز.

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- يتم تبخير العينة حتى تتصاعد الأبخرة البيضاء SO3.
- يتم إضافة ١٠ مللى من حمض النيتريك لاذابة الرواسب.
- يجب الخلص من حمض التيتريك تهائيا بواسطة التسخين المتمر حتى يصبح المحلول رائق وخاليا من الأبخرة البنية.
- تبرد العينة وبكمل الحجم الى ٥٠ مللى
- يسخن المحلول الى درجة الغليان لاذابة الاملاح بطيئة الذوبان يتم ترشيح العينة اذا لزم الامر.
- ينقل الراشح الى دورق معيارى سعة ١٠٠ مللى على مرتين ب ٥ مللى من الماء المقطر.
- يترك المحلول ليبرد ثم يكمل الحجم الى العلامة ويمزج جيدا.

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AAS - ATOMIC ABSORPTION SPECTROMETRY (SCOPY)

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AAS - ATOMIC ABSORPTION SPECTROMETRY (SCOPY)

- **Atomic absorption is a process involving the absorption by free atoms of an element of light at a wavelength specific to that element or put, i.e. a means by which the concentration of metals can be measures.**
- **When a sample or sample solution is burned in a flame or heated in tube, the individual atoms of the sample are released to form a cloud inside the flame or tube**

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- **Each atom consists of a positively charged nucleus surrounded by a number of electrons in rapid motion around the nucleus.**
- **For each electron in each atom there is a discrete set of energy levels that electron can occupy.**
- **The spacing of the energy levels is different for each electron in the atom, but for similar corresponding electrons have identical spacing.**
- **For an unexcited atom, each electron is in the ground state. To excite the atom, one or more electron can be raised to the first or higher energy levels by absorption of energy by the atom. This energy can be supplied by photons or by collisions due to heat**

- Those electrons furthest from the nucleus require least energy to go from the ground state E0 to the first energy level E1.
- The energy E corresponds to the energy gap between the ground state and the first energy level.

  $E = E1 - E0$
- The energy required for this transition can be supplied by a photon of light with an energy given by:

  $E = h\nu$, where h = Planck's constant and ν the frequency.
- This corresponds to a wavelength (λ) of

  $(\lambda) = hc/E$
- Where, c is the speed of light in vacuum.

- Metallic and metalloid elements, contain so called valence electrons which are relatively loosely bound to the nucleus and which can be excited by photons of wavelengths in the optical range 190 – 900 nm,
- For each atom of a metal or metalloid the energy gap is not found in any other element.
- If light of sufficiency narrow wavelength rage, centred on $hc/ E1 - E0$ is sent through a cloud of various atoms, only atoms of one particular element will absorb photons.
- Hence the selectively of the atomic absorption technique.

- **Atoms in the cloud move at high speed and collide with each other, and absorb over a narrow range of wavelengths.**
- **The width of a typical absorption line is about 0.001nm.**
- **For atomic absorption instrument purposes, an emission source with an emission line of the same frequency and a width of about 0.001 nm is normally used.**
- **This requirement is satisfied by an emission spectrum of the element of interest, generated by hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).**

- **That's why the light source used in the measurements is the emission source of the element to be determined**
- **AAS-apparatus measures the amount of absorption and this is directly proportional to the free atoms which are in way of the light beam**
- **By comparing the absorbance of the unknown sample solution to the absorbance obtained with standard solutions (using the same conditions) you can get the metal concentration of the sample solution**

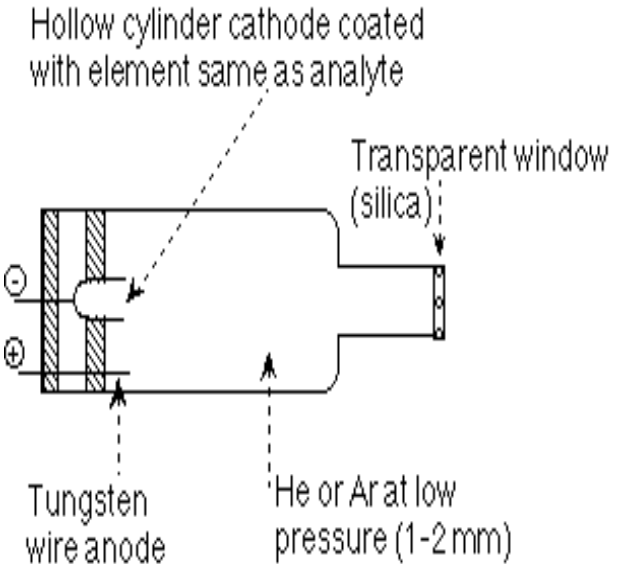
There are three basic components for every AA spectrophotometer:

1. Light source :

It is designed to emit the atomic spectrum of a particular element. Specific lamps are selected according to the element to be determined.

The hollow cathode lamp (HCL) or electrode less lamps (EDL) are widely used.

The hollow cathode lamp (HCL)

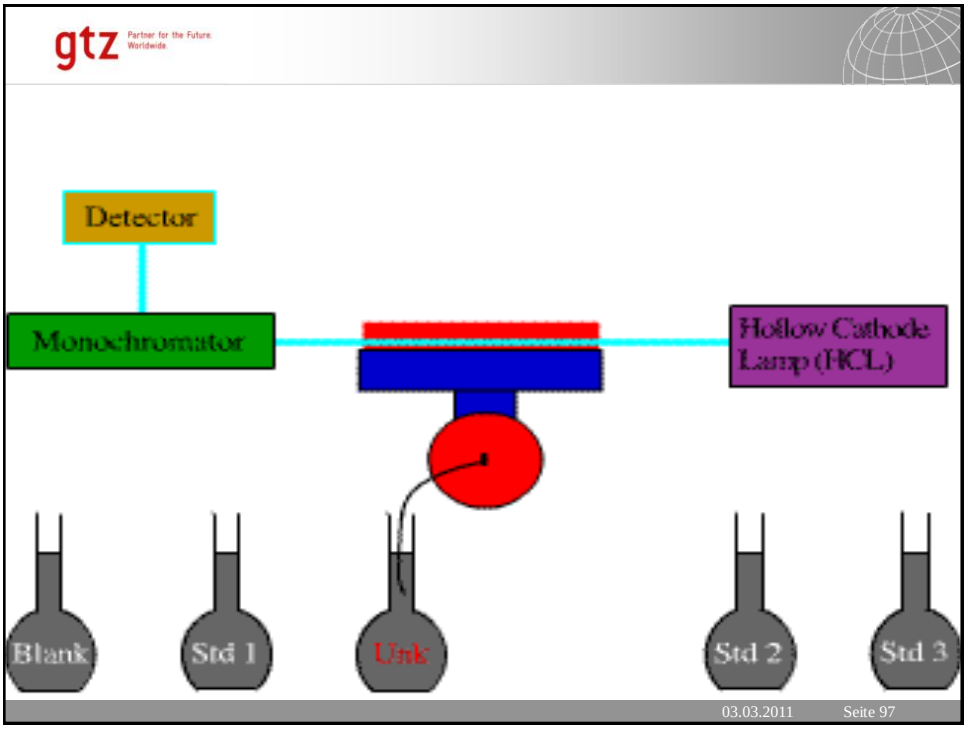


2. Sample cell :

Where an atomic sample vapor is generated in the light beam from the source. This is usually done by introducing the sample into a burner system (Flame AAS) or electrically heated furnace or platform, aligned in the optical path of the spectrophotometer.

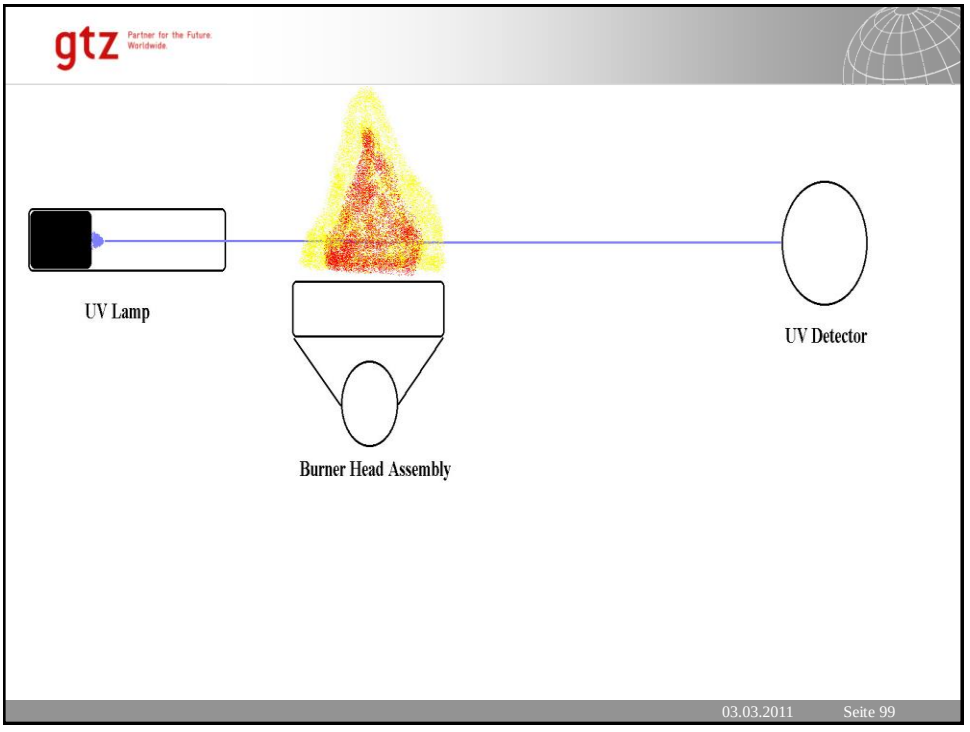
3. Specific light measurement - Includes several components:

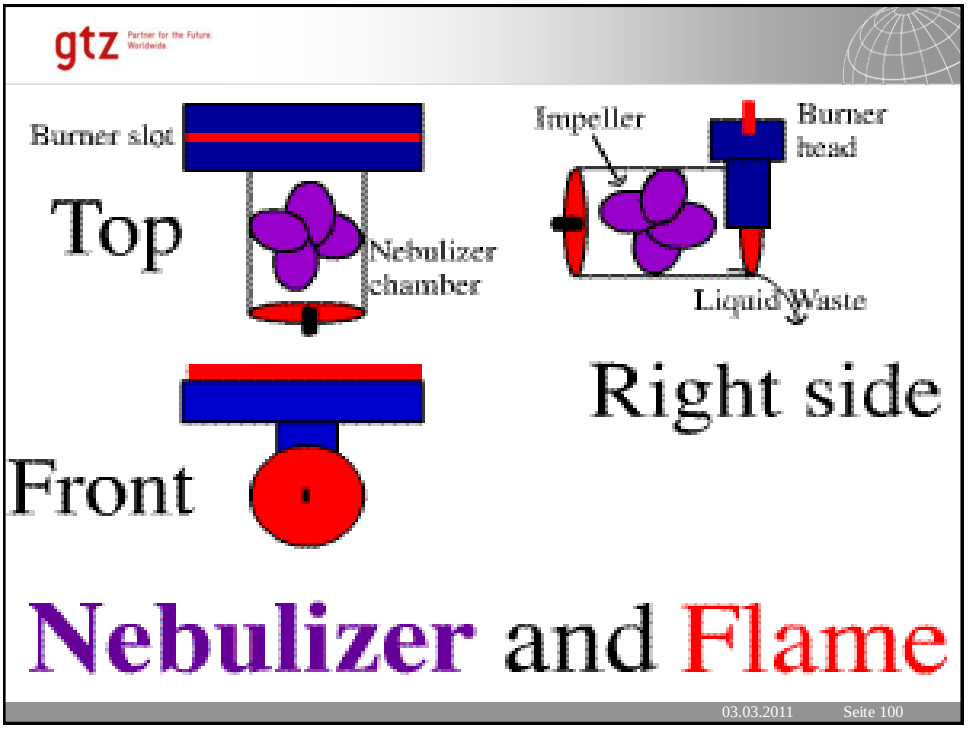
a) A monochromator to disperse several wavelength of lights that are emitted from the light source to isolate a particular line of interest,



b) A detector to produce an electrical current that is dependent on the light intensity. This electrical current is amplified and processed by the instrument electronics to produce a signal, which is a measure of the light attenuation occurring in the sample cell and,

c) This signal is further processed to generate an instrument readout in concentration units.


UV Lamp
Burner Head Assembly
UV Detector
03.03.2011 Seite 99


Burner slot
Top
Nebulizer chamber
Impeller
Burner head
Liquid Waste
Right side
Front
Nebulizer and Flame
03.03.2011 Seite 100

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Different AAS- techniques :

Flame technique :

- It converts the sample solution into an atomic vapour and then thermally elevates the atoms to an excited state.

- These atoms return to the ground state they emit light, which detected by the instruments

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- The intensity of light is related to the concentration of the elements in the solution.
- Air-acelylene flame about 2200 °C
- Suitable for most elements
- Nitrous oxide (N2O-acetylene flame about 2600 °C)
- Used for difficult atomizing elements like Sn, Al, Ba

Non flame techniques:

Graphite furnace technique

- Atomization with heating electrically
- About 100 times as sensitive as flame technique
- The graphite cylinder is heated by the passage of an electric current to the temperature, which is enough to evaporate the solvent from the solution
- The current is then increased so that firstly the sample is ashed and then it is vaporized and the metal atom are produced in the solution.

Cold vapour technique (for Hg).

Hydride generation method:

- This technique makes use of the property that the metalloid elements (i.e As, Se, Sb, Bi, Se, Te, Ge , Hg, and Pb) exhibit, i.e. the formation of covalent, gaseous hydrides which are not very stable at high temperatures..

- **The hydrides of arsenic, selenium, tellurium, antimony, bismuth and tin (and to lesser degree lead and germanium) are volatilized by the addition of reducing agent like sodium tetrahydroborate (III) to an acidified solution. Other systems have used titanium (III) chloride/magnesium powder and tin (II) chloride/potassium iodide/zinc powder as reducing agents.**

- **Sodium tetrahydroborate (III) is the preferred method because it gives faster hydride formation, higher conversion efficiency, lower blank levels and is more simple to use.**

The principle of the hydride generation method is shown as follows using selenium as an example:

- **Se4+ (Aq) + BH4- (aq) + H+ → H2 Se (g) ↑ + H 2 (g)↑ + H3 BO3**
- **H2Se (g) → Se (g) + H (g)**
- **Mercury is reduced to the atomic form in a similar manner**

- **After the gaseous hydride is formed it is passed, together with any excess hydrogen gas, to the atomizer mounted in the optical path of the spectrometer.**
- **In case of As determination, the flame is required the flowing flames are suitable for use with the flame heated T-cell: Air/Acetylene, argon/hydrogen, air/ hydrogen, nitrogen/hydrogen. However, Nitrous oxide/acetylene and nitrous oxide/ hydrogen flames must never be used to heat the T- cell.**

Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS)

Introduction:

- **Graphite furnace atomic absorption spectroscopy (GF-AAS) is a powerful technique suitable for trace analysis.**
- **The technique has high sensitivity.**
- **The ability to handle micro samples (5-100 ml) and a low noise level from the furnace.**
- **Matrix effects from components in the sample other than the analyte are more severe in this technique compared to flame-AAS.**

Principles:

- A graphite tube is located in the sample compartment of an AA spectrometer with the light from an external light source passing through it.
- A small volume of sample is placed inside the tube, which then is heated by applying a voltage across its ends.

- The analyte is dissociated from its chemical bonds and the fraction of analyte atoms in the ground state will absorb portions of light.
- The attenuation of the light beam is measured.
- As the analyte atoms are created and diffuse out of the tube, the absorption raises and falls in a peak-shaped signal.
- Beer-Lamberts law describes the relation between the measured attenuation and concentration of analyte.

GRAPHITE TUBES (FURNACES)

1. **Standard tube = normal graphite**
2. **pyrolytically coated tube:**
   1) **the sample disperses (scatters) more even**
   2) **the formation of carbides decreases**
   3) **the service life increases**
   4) **the atomic vapour doesn't go through the walls of tube.**
3. **Tube with platform: (L'vov's platform)**
   1) **temperature more stable**
   2) **the speed of heating is great (for platform)**
   3) **it is usable for easily volitilizing elements**

Things which effect to the service life of tube

1) **temperatures**
2) **atomization time**
3) **matrix quality (acids, solids)**
4) **physico-chemical characters of matrix**

MATRIC MODIFICATION IN GFAAS

- To find the optimal parameters in measurements:

  1) as high ashing temperature as possible

  2) as low atomization " " "

- It is not always possible to use ashing temperature high enough

- Without loss (volatilation) of the element

The idea in using matrix modifiers is:

1) the volatilization of the element to be determined decreases and the great part of the matrix disappears or

2) the vitalization of the matrix increases and the disturbing^ compounds eliminate before the atomization of the element to be determined

EXAMPLES

- As volatilizes at 200 °C, Ni is added —> Ni-arsenid decomposes >

1200 °C —> the ashing temperature may raised to 1200 °C

- high CI-concentration in the sample solution —> disturbances in

Pb and Cd measurements, add NH4H2P04 -> NH4Cl

Interference:

1. Background absorption:

- **Background absorption is non-specific attenuation of radiation at the analyte wavelength caused by matrix components.**
- **Enhanced matrix removal due to matrix modification may reduce background absorption.**
- **To compensate for background absorption, correction techniques such as continuous light source (D2-lamp), Zeeman or Smith-Hieftje should be used.**

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Background Correction methods

- **The narrow bandwidth of hollow cathode lamps make spectral overlap rare. That is, it is unlikely that an absorption line from one element will overlap with another .**
- **Molecular emission is much broader, so it is more likely that some molecular absorption band will overlap with an atomic line. This can result in artificially high absorption and an improperly high calculation for the concentration in the solution .**

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Three methods are typically used to correct for this:

1.Zeeman correction :

- **A magnetic field is used to split the atomic line into two sidebands . These sidebands are close enough to the original wavelength to still overlap with molecular bands, but are far enough not to overlap with the atomic bands. The absorption in the presence and absence of a magnetic field can be compared, the difference being the atomic absorption of interest .**

2.Smith-Hieftje correction:

The hollow cathode lamp is pulsed with high current, causing a larger atom population and self-absorption during the pulses. This self-absorption causes a broadening of the line and a reduction of the line intensity at the original wavelength .

3. Deuterium lamp correction :

- **In this case, a separate source)a deuterium lamp) with broad emission is used to measure the background emission .**
- **The use of a separate lamp makes this method the least accurate, but its relative simplicity**
- **The fact that it is the oldest of the three, makes it the most commonly used method .**

2.Non-spectral interference (Matrix effect):

- **Non-spectral interference arises when components of the sample matrix alter the vaporization behaviour of the particles that contains the analyte.**
- **To compensate for this kind of interference, method of standard addition can be used.**
- **Enhanced matrix removal by matrix modification or the use of a L´vov platform may also lead to a reduction of non-spectral interferences.**

Instrumentation:

- **Atomic absorption spectrophotometer single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, equipment for flameless atomization (graphite furnace) and a suitable recorder or PC. The wavelength range must be 190-800 nm.**
- **Hollow cathode lamps for As, Cu, Cr, Ni, Pb and Zn. Single-element lamps are preferred, but multi-element lamps may be used if no spectral interference can occur. Electrodeless discharge lamps may be used if available.**
- **Pyrolytically coated graphite tubes.**

Setting up a temperature programme:

- A temperature programme consists most commonly of four steps: Drying, pyrolysis, atomization and cleaning.

1. Drying step:

- A quick ramp (5 s) to 15oC below the boiling point of the solvent. Then a slow ramp (25 s) to reach a temperature just above the solvents boiling point.
- This provides a gentle evaporation without sputtering.
- Hold the furnace at the selected temperature until drying is complete (5- 10 s).
- The drying time will vary with sample volume and salt content.
- A purge gas flow of 250-300 ml min-1 is normally used.

2. Pyrolysis step:

- A pyrolysis curve should be made to find the appropriate temperature to use in this step without losing any analyte.
- Consult the instrument manual for the procedure of making a pyrolysis curve.
- In a pyrolysis step a typical ramp will vary between 20-50 oC/s.
- Too steep ramp may cause sputtering. A purge gas flow of 250-300 ml min-1 is normally used.

3. Atomization step:

- An atomization curve should be made to find the appropriate temperature to use in this step.
- Consult the instrument manual for the procedure of making an atomization curve.
- The lowest temperature that still gives maximum signal should be used in order to extend the lifetime of the graphite tube.
- Zero ramp time is used in this step. Gas stop during atomization is recommended.

4.Cleaning step:

- A tube cleaning cycle after the analyte measurement should be done to remove any remains of sample and thereby avoid memory effects.

- A purge gas flow of 250-300 ml min-1 is normally used.

Instrument performance:

- The characteristic mass (sometimes called sensitivity) is defined as: The absolute mass of an element that will absorb 1% of the incoming radiation. This equals a signal of 0.0044 absorbance units (AU).

The characteristic mass may be used as an indicator of instrument optimization.

- Values of the characteristic masses are most often given in the instrument documentation.
- Experimental values for comparison can be determined by measuring the absorbance signal (area) of a known mass of analyte and calculate using the following formula:

mo = Vs * Cs*0.0044 AU / observed peak area

mo: Characteristic mass (ng)

Vs: Standard volume injected (ml)

Cs : Standard concentration (ng ml-1)

Chemical modifiers:

- In order to achieve better separation between analyte and matrix prior to atomization, a chemical modifier can be used.

- The role of the modifier is most often to stabilise the analyte making higher temperatures in the pyrolysis step possible without any loss of analyte.

- The concentration level of most modifier mixtures is usually in the ppm level.
- The injection volume most often is in the 5-20 µl region.
- The modifier mixture should be injected and dried prior to sample injection.

Sequence of analysis

- Start the analysis with an “empty tube” run.
  - If a significant signal is obtained, a cleaning step (2650oC, 2-3 s) should be run repetitively to remove the remains in the tube.
  - If this is not sufficient, the graphite tube should be replaced.
- The chemical modifier solution (if used) should be checked for contamination in a separate run.
- The blank solution should be analyzed to establish a blank

- **In addition to the blank standard, at least 3 standards should be selected to cover the linear range.**
- **Repeat the analysis until good agreement between replicates and a linear calibration curve is obtained.**
- **A quality control standard should be analyzed to verify the calibration.**

- **Samples that are found to have concentration higher than the highest standard should be diluted into range and reanalyzed.**
- **To monitor the performance of the graphite tube, a mid-level standard and a blank standard should be run after every 10th sample.**

Flame atomic absorption spectroscopy (F-AAS)

- **Introduction**
  - **F-AAS is a very specific technique prone to few interference effects.**
  - **F-AAS is a single element technique with analyte determinations in the mg l-1 region as routine for most elements.**

- **Principles**
  - **A liquid sample is nebulized to form a fine aerosol, which is mixed with fuel and oxidant gasses and carried into a flame.**
  - **In the flame the sample is dissociated into free ground state atoms.**
  - **A light beam from an external light source emitting specific wavelengths passes through the flame.**

- The wavelength is chosen to correspond with the absorption energy of the ground state atoms of the desired element.
- The measured parameter in F-AAS is attenuation of light.
- Lambert-Beers law expresses the relationship between the attenuation of light and concentration of analyte.

2. Principles:

- A liquid sample is nebulized to form a fine aerosol, which is mixed with fuel and oxidant gasses and carried into a flame.
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- **The wavelength is chosen to correspond with the absorption energy of the ground state atoms of the desired element.**

- **The measured parameter in F-AAS is attenuation of light.**

- **Lambert-Beers law expresses the relationship between the attenuation of light and concentration of analyte.**

Interferences:

- **F-AAS is known as a technique with few problems related to interference effects.**

- **The interferences that occur are well defined, as are the means of dealing with them.**

- **For analysis of a few elements the type and temperature of the flame are critical; with improper conditions ionization and chemical interferences may occur.**

Ionization:

- Ionization of the analyte atoms in the flame depletes the levels of free ground state atoms available for light absorption.
- This will reduce the atomic absorption at the resonance wavelength and lead to erroneous results.
- The degree of ionization of a metal is strongly influenced by the presence of other invisible metals in the flame.

- By addition of an excess of a very easily ionized element to the blanks, standards and samples the effect of ionization can usually be eliminated.
- Ionisation is most common in hot flames such as nitrous oxide- acetylene flames.
- In an acetylene-air flame ionization is most often limited to be a problem in analysis of the alkali- and alkaline earth metals.

Chemical interference:

- The most common type of chemical interference occurs when the sample contains components that forms thermally stable compounds with the analyte and thus reduce the rate at which it is atomised.

- Adding an excess of a compound that form thermally stable compounds with the interfering element eliminates chemical interference.

- For example, calcium phosphate does not dissociate completely in the flame. Addition of Lanthanum will tie up the phosphate allowing calcium to be atomised.

- A second approach to avoid chemical interference is, if possible, to use a hotter flame.

- Using the method of standard addition can also control chemical interference.

Physical interference:

- If the physical properties as viscosity and surface tension vary considerably between samples and standards, the sample uptake rate or nebulization efficiency may be different and lead to erroneous results.

- Dilution of samples or method of standard addition or both can be used to control these types of interferences. .

Background absorption and light scattering:

- Matrix components that are not 100% atomised and that has broadband absorption spectra may absorb at the analytical wavelength.
- Tiny solid particles in the flame may lead to scattering of the light over a wide wavelength region.
- The background absorption can be accounted for by using background correction techniques such as continuous light source (D2-lamp) or Smith-Hieftje.

Instrumentation:

- Atomic absorption spectrophotometer single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, equipped with a air-acetylene burner head and a suitable recorder or PC.

- The wavelength range must be 190-800 nm.

Calibration standards:

- Calibration standards are prepared by single or multiple dilutions of the stock metal solution.
- Prepare a reagent blank and at least 3 calibration standards in graduated amount in the appropriate range of the linear part of the curve.
- The calibration standards must contain the same acid concentration as will result in the samples following processing.
- For precipitation samples, that would be 1% (v/v) HNO3 and for suspended particulate matter10% (v/v) HNO3.
- The calibration standard should be transferred to polyethylene bottles.

Instrumental procedure:

- **The operating procedure will vary between instrument brands, so the instrument manual should be followed carefully.**
- **The position of observation and the fuel: oxidant ratio must be optimised.**
- **Some general guidelines are outlined below**

- **Light the hollow cathode lamp or electrode discharge lamp and D2-lamp if such background correction is used.**
- **Set the lamp current to the value specified by the manufacturer.**
- **Position the monocromator at wavelength 213.9 and choose slit with 0.7 and slit height “high”.**

- **Carefully balance the intensity of the hollow cathode lamp and the D2-lamp if such background correction is used.**
- **Align the burner head to assure that the centre of the light beam passes over the burner slot.**
- **Light the flame and regulate the flow of fuel and oxidant to produce an oxidizing flame (lean blue).**
- **Aspirate calibration blank and establish a zero point.**
- **Aspirate standard solutions and construct a calibration curve.**
- **Aspirate distilled water after each standard or sample.**

Instrument performance:

- **The "characteristic concentration" (sometimes called sensitivity) is defined as the concentration of an element (mg l-1) that will absorb 1 % of the incoming radiation. This equals a signal of 0.0044 absorbance units (AU). The "characteristic concentration" is instrument dependent and is calculated as follows:**

  C = (S * 0.0044 AU) / measured absorbance

  C: Characteristic concentration (mg l-1)

  S: Concentration of measured standard (mg l-1)

- **Knowing the "characteristic concentration" allows the analyst to check if the instrument is correctly optimized and performing up to specifications.**

Sequence of analysis:

- Aspirate calibration blank and establish a blank level
- Aspirate calibration blank and standard solutions and construct a calibration curve. Use at least 3 standard solutions in addition to the calibration blank to cover the linear range. Every point at the calibration curve should, if possible, be based on replicate analysis. Distilled water should be aspirated after each standard and sample.

- A quality control standard should be analysed to verify the calibration.
- A calibration blank should be analysed to check for memory effects.
- Aspirate unknown samples.
- Aspirate a quality control standard for every 10th sample to check for drift.
- Samples that are found to have concentration higher than the highest standard should be diluted and reanalyzed.

LAMPS FOR AAS

1.Hollow cathode lamp (HCL):

- suitable for most elements (discharge lamp)
- the cathode is made about the element to be determined
- for certain elements short-lived because of the volatilazion (e.g. As, Se)
- cheapness

2.Electrode less discharge lamp (EDL):

- longer durability for most elements greater sensitivity and stability
- need their own power supply
- expensive

Hollow Cathode Lamps

- Hollow cathode lamps are the most widely used radiation sources in the AA technique.
- A hollow cathode lamp consists of a glass cylinder, and an anode and a cathode. The cylindrical cathode is either made of the analyte element or filled with it.
- The diameter of the cathode is 3 to 5 mm.

- The anode is in the form of a thick wire and usually made of tungsten, nickel, tantalum, or zirconium.
- The glass tube is first evacuated and then filled with an inert gas (argon or neon).
- The pressure of the inert gas is about 0.5 to 1.3 kPa

Hydride Generation Analysis

- **Hydride generation – elements which form gaseous hydrides: Sb, As, Bi, Se, Te, Sn - HGAAS**
- **Hg – Cold Vapour, CVAAS**
- **Acidified sample solution is reacted with NaBH4 producing the analyte hydride, which is carried on a stream of argon carrier gas to the atomizer**
- **The hydride decomposes in the atomizer to the elemental form and can be measured**

- **A number of elements such as arsenic and selenium form volatile hydrides on reduction of their salts with suitable reducing agents such as sodium borohydride.**
- **Atomic absorption of the free atoms of the analyte element then occurs in the same way as with the flame or with an electrically heated cell.**
- **Mercury can be determined in the same way but in this case the inorganic mecury present in the samples is reduced to atomic mercury, which can then be swept into the absorption tube where the atomic absorption process occurs.**

- This analysis the tube does not need to be heated as the free atoms are generated at room temperature.Hence the name Cold Vapour AAS.
- **The basic theory is that:**
  - the acidified sample solution is reacted with NaBH4 producing the analyte hydride, which is carried on a stream of argon carrier gas to the atomizer.
  - The hydride decomposes in the atomizer to the elemental form and can be measured

Now for the science---------

- Acidify sample
- Mix with reluctant
- Sodium borohydride NaBH4
- Analyte reduced to gaseous hydride

$As^{3+} + BH_4^- + H^+ \rightarrow AsH_3\ (gas) + BO_3 + H_2$

- Gaseous analyte hydride separated from liquid reagents
- Gas liquid separator device
- Gaseous analyte hydride carried into heated cell
- Inert (e.g. Ar, N2) used to transport it
- Analyte atomised, and AA signal measured

Hydride V's Flame

- **Reasons for poor flame sensitivity for hydride group elements:**
  - **Low intensity HCL's**
  - **Absorption by flame gases**
  - **Inefficiencies in sample intro eg. Nebulisation**
  - **Improved sensitivity and reduced noise result in detection limits typically 1000x better than those achieved by conventional flame analysis.**

- **The primary resonance lines used to measure the hydride group elements are in the deep UV region of the spectrum – indeed, the primary arsenic and selenium lines are below 200nm.**
  - ➢ **In this region of the spectrum, the normal flame gases, and even the air itself, will absorb a significant proportion of the radiation emitted by the lamp.**

➢ **This combination of low intensity hollow cathode lamps and the absorption by the flame gases results in rather noisy absorption signals, and consequently poor detection limits.**

- **Hydride generation offers the opportunity to improve sensitivity and reduce noise resulting in improved detection limits, which are typically 1000x better than those achieved by conventional flame AAS.**

Typical Environmental applications:

- **As in drinking water**
- **Se in wastewaters**
- **Hg in soils and sludges**
- **As in seawater**
- **Hg in drinking water**

Vapour Generation - Modes of Operation

Vapour Generation accessories can be designed in 3 ways:

1) Batch Operation
2) Flow Injection
3) Continuous Flow

1) Batch Operation

- Discrete portions of reagents are mixed with each sample
- Volatile hydrides generated are swept into the spectrometer for measurement.
- The signal is measured as a peak

Benefits:

1. The hardware required is cheap and simple.
2. Detection limits can be good, as large volumes of sample can be used.
3. No software interface is required.

Drawbacks:

1. Sample throughput rate is low.
2. It is next to impossible to automate the measurement.
3. It is extremely difficult to interface the device to an autosampler.
4. Reagent consumption is high.
5. Significant operator skill and dexterity is required..

2) Flow Injection Operation

- A peristaltic pump is used to generate continuously flowing streams of reagents.
- A 6 port valve and sampling loop are used to inject discrete portions of the sample into one of the reagent streams.
- The reagent streams are mixed, and the volatile hydrides are separated in a gas liquid separator and transported to the spectrometer for measurement.
- The signal is measured as a peak

3) Continuous Flow

- Reagents and sample are pumped to a reactor zone, where the chemical reaction takes place.
- The volatile hydrides are separated from the reaction mixture in a gas-liquid separator, and transported to the spectrometer for measurements.
- The signal rises to a steady state value, and can be integrated for as long as desired.

Benefits:

- The hardware required is reasonably simple. Signal precision is good.
- Fully automatic operation is possible eg. auto samplers. Sample throughput rate is moderate.
- Reagent consumption is moderate.

Drawbacks:

- Sensitivity is limited by maximum sample flow rate.
- Significant (>10 seconds) stabilization and wash through times are necessary to avoid memory effects.
- A software interface may be required.
- The design of the gas liquid separator is critical, and must be optimised empirically

Sample Preparation Issues:

- Sample preparation is a key issue with hydride generation analyses.
  - Sample pre-reduction requirements can be divided, as you would expect into their respective groupings on the periodic table.

- **Group VI elements Se and Te always require prereduction to the tetravalent state, since the hexavalent oxidation state for both elements would result in no measurable signal by any configuration.**

- **Group VI - Se and Te require pre-reduction adding /boiling solutions with HCl for ~10 mins**

- **Group V (As,Sb and Bi) require pre-reduction**
  - **usually achieved using either Potassium Iodide or L-Cysteine**
- **Mercury requires no special prereduction sample preparation,**
  - **But the actual reduction of mercury can take place through two reaction mechanisms:**

1. **Sodium Borohydride (NaBH4)**
2. **Stannous Chloride (SnCl2)**

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Ion Coupled Plasma

ICP

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An inductively coupled plasma (ICP)

- ICP is a type of plasma source in which the energy is supplied by electrical currents which are produced by electromagnetic induction, that is, by time-varying magnetic fields

- **Plasma** refers to an ionized gas, in which a certain proportion of electrons are free, rather than being bound to an atom or molecule.

  - The ability of the positive and negative charges to move somewhat independently makes the plasma electrically conductive so that it responds strongly to electromagnetic fields .

- Plasma therefore has properties quite unlike those of solids, liquids or gases and is considered to be a distinct state of matter .

- Plasma typically takes the form of neutral gas-like clouds)e.g .Stars)

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Operation:

- **There are two types of ICP geometries:** planar and cylindrical.
  - In planar geometry, the electrode is a coil of flat metal wound like a spiral .
  - In cylindrical geometry, it is like a helical spring.
  - When a time-varying electric current is passed through the coil, it creates a time varying magnetic field around it, which in turn induces azimuthal electric currents in the rarefied gas, leading to break down and formation of plasma .
  - Argon is one example of a commonly used rarefied gas.

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- **Plasma temperatures** can range between 6000K and 10000K , comparable to the surface of the sun
- ICP discharges are of relatively high electron density, on the order of 1015 cm-0.3
- As a result, ICP discharges have wide applications where a high density plasma is necessary.

- **Another benefit of ICP discharges is that they are relatively free of contamination because the electrodes are completely outside the reaction chamber.**

- **In a capacitively coupled plasma (CCP), in contrast, the electrodes are often placed inside the reactor and are thus exposed to the plasma and subsequent reactive chemical species.**

Applications:

- **ICP-AES, a type of atomic emission spectrometry**
- **ICP-MS, a type of mass spectrometry .**
- **ICP-RIE, a type of reactive ion etching .**

Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

- Also, referred to as Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is an analytical technique used for the detection of trace metals.
- It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element .

- The intensity of this emission is indicative of the concentration of the element within the sample.

The ICP-OES is composed of two parts:

1. The ICP and
2. The optical spectrometer .

The ICP torch consists of 3 concentric quartz glass tubes .

- A water cooled coil of a radio frequency (RF) generator which surrounds part of the torch .
- Argon gas is typically used to create the plasma.

- When the torch is turned on, an intense magnetic field from the radio frequency (RF) generator is turned on .
- The argon gas flowing through is ignited with a Tesla unit (typically a copper strip on the outside of the tube)

- The argon gas is ionized in this field and flows in a particular rotationally symmetrically pattern towards the magnetic field of the RF coil .
- A stable, high temperature plasma of about 7000K is then generated as the result of the inelastic collisions created between the neutral argon atoms and the charged particles

A.Peristaltic pump

- **Delivers an aqueous or organic sample into a nebulizer where it is atomized and introduced directly inside the plasma flame .**
- **The sample immediately collides with the electrons and other charged ions in the plasma and is broken down into charged ions .**

- **The various molecules break up into their respective atoms which then lose electrons and recombine repeatedly in the plasma, giving off the characteristic wavelengths of the elements involved.**

- A shear gas, typically nitrogen or dry compressed air is used to 'cut' the plasma flame at a specific spot .1 or 2 transfer lenses are then used to focus the emitted light on a diffraction grating where it is separated into its component radiation in the optical spectrometer .

- The light intensity is then measured with a photomultiplier tube at the specific wavelength for each element line involved.
- The intensity of each line is then compared to previous measured intensities of known concentrations of the element and its concentration is then computed by extrapolation along the calibration line.

التحقق من صحة النتائج

Quality Control

مقدمة:

مسئولية ضمان الجودة فى المعامل تنسب الي شخص له خبرة كافية ببرامج ضمان الجودة وكيفية أدارتة وتحديثه ولديه السلطة والمسئولية لتطبيق برنامج ضمان الجودة، وذو مركز يتيح له الاتصال بالإدارة العليا لنقل التقارير إليها.

مسئول ضمان الجودة يجب أن تعليمه عمليا Technical education ، مطلع على كل النواحي المعملية، وعلى علم بالطرق الإحصائية لتقييم النتائج. مسئول ضمان الجودة يقوم على إدخال البرنامج وتحديثها، إقناع الأعضاء بأهميته، وتقديم المعلومات الضرورية والتدريب لكل أعضاء المعمل

تعريفات Definitions

- **حزمة الأستخلاص:Extraction Batch**
  - **هي مجموعة من العينات الحقلية يتم أستخلاصها تحت نفس الظروف وبنفس الشخص خلال يوم عمل واحد ويستخدم محلول قياسي واحد لجميع العينات. وهذه المجموعة من العينات تحتاج الي عينات ضابطة**
- **حزمة التحاليل:Analysis Batch**
  - **عبارة عن مجموعة من العينات يتم تحليله تحت نفس الظروف خلال ٢٤ ساعة متضمنة أختبار عملية المعايرة: Calibration check standards (CCC)**

تابع تعريفات Definitions

- **المحاليل القياسية:**
- **Standard Solutions**
- **محلول قياسي مركز: Stock Standard Solution (SSS)**

محلول قياسي مركز يحتوي علي العنصر المراد قياسة في المعمل.

ويمكن شرائة من جهات معتمدة وتركيزه غالبا ١٠٠٠ ملجم/ لتر.

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تابع تعريفات Definitions

محلول قياسي أولي: Primary Dilution Standard (PDS) Solution

يحضر من المحاليل المركزه Stock Standard Solution (SSS) ويخفف بنفس المذيب المستحدم في تحضير المحلول المركز الي تركيز متوسط مابين المركز والعياري.Calibration Standard (CAL)

محلول قياسي عياري: Calibration Standard (CAL)

يحضر من الحلول القياسي الأولي(PDS) والعياري البديل(SUR) والقياسي الداخلي(IS) وذلك لمعايرة الجهاز وتحديد كفاءته وحساب تراكيز المكونات

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Definitions تابع تعريفات

ضابط الكواشف المعملية: Laboratory Reagent Blank (LRB)

- يحضر للتعرف علي وجود أي شوائب أوتدخلات بالعينة خلال عملية تناول ومعالجة العينة. ويتم تحضيره بإختبار حجم من المياه الخالية من المواد العضوية مساوي لحجم العينة المراد تحليلها ويتم التعامل معها كعينة.
- إذا زاد تركيز العنصر المراد قياسة فى عينة البلانك عن حد التقدير لطريقة التحليل فإن هذا يشير الى وجود تلوث إما ان يكون ناتج من الكواشف أو من الادوات المستخدمة فى التحليل.
- يجب تحليل عينة بلانك عند تحليل مجموعة من العينات (٢٠ عينة أو أقل).

Definitions تابع تعريفات

- **ضابط للتأكد من جودة المعمل: Laboratory Fortified Blank (LFB)**

يحضر بإضافة المكونات المراد قياسها الي ١ لتر من الماء الخالي من الملوثات العضوية ويتم أجراء التحاليل الازمة كعينة تماما ، ومن النتائج المتحصل عليها يمكن التعرف علي جودة ودفة التحاليل.

يجب تحليل عينة (LFB) عند تحليل مجموعة من العينات (٢٠ عينة أو أقل).

Definitions تابع تعريفات

- **عينة حقلي مضاف اليه المكونات للتحقق من صحة النتائج: Laboratory Fortified Sample Matrix (LFSM**

- **عينة حقلية مضاف اليها العناصر المراد تحليلها Known quantities of the method analytes تحت نفس ظروف ومواصفات العينة . ويتم حساب معدل الإسترجاع ورسم control charts وحساب control limits للنتائج. ومن النتائج المتحصل عليها يمكن التعرف علي جودة ودفة التحاليل وذلك لتحديد كفاءة ودقة المعمل، مكونات العينة يجب قياسها واعتبارها القاعدة الأساسية عند الحساب.**
- **يجب تحليل عينة (LFSM) عند تحليل مجموعة من العينات (٢٠ عينة أو أقل).**

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Definitions تابع تعريفات

- **ضابط معملي مذدوج: Laboratory Fortified Sample Matrix Duplicate (LFSMD)**

تقسم عينة حقلية المضاف اليه العنصر للتحقق من صحة النتائج الي نصفين متساوين تماما، ويتم تحليلهما تحت نفس الظروف وبنفس الطريقة والمواصفات ومن نتائج التحاليل يمكن التأكد من صحة النتائج.

- **عينة مرجعية للتحقق من صحة النتائج: Quality Control Sample (QCS)**

تحضر في المعمل من المحاليل القياسية الأولية ويمكن الحصول عليها من جهات معتمدة (EPA- UNEP)

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تابع تعريفات Definitions

- **الحد الأدنى للطريقة: Detection Limit(DL)**

أقل تركيز للمكونات المراد قياسها مع التأكد ٩٩% من أن يكون التركيز أكبر من الصفر.

- **أقل تركيز يعتمد في التقرير: Minimum Reporting Level (MRL)**

أقل تركيز يمكن تعينه ويشترط يكون أكبر من أن أقل تركيز للمحاليل القياسية العيارية

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خطوات التحقق من صحة النتائج
Quality Control Procedure

- يجب علي المعامل المسئولة علي القيام بالتحاليل الخاصة بالملوثات العضوية الشحيحة اتباع برامج التحكم في جودة ودقة التحاليل بحيث تشتمل علي التقيم الأولي لقدرة المعامل، التأكد من أن كل حزمة تحاليل تشتمل علي جميع الضوابط والمحاليل العيارية والقياسية.

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- مسئولية ضمان الجودة فى المعامل تنسب الي شخص له خبرة كافية ببرامج ضمان الجودة وكيفية أدارتة وتحديثه ولديه السلطة والمسئولية لتطبيق برنامج ضمان الجودة، وذو مركز يتيح له الاتصال بالإدارة العليا لنقل التقارير إليها.
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التقيم المبدئي للمختبر
Initial Demonstration of Capability (IDC)

التقيم المبدئي للتعرف علي تركيز الشوائب:

Initial Demonstration of Low System Background

للتأكد من خلو الكواشف من أي شوائب أو للتعرف علي التركيز المرجعي(background concentration) وذلك بتحليل عينة ضابط الكواشف المعملية Laboratory reagent blank والتأكد من خلو الكواشف من أي شوائب.

تابع التقيم المبدئي للمختبر
Initial Demonstration of Capability (IDC)

Initial Demonstration of Accuracy: التقيم المبدئي للجودة

- **وذلك بتحليل عينة مرجعية معلومة التركيز ويجب أن تكون نتيجة التحليل مابين ٨٠% ، ١٢٠% من التركيز الأصلي.**
- **بعد التاكد من التحاليل السابقة يتم تحليل عينة ضابط معملي تحتوي علي تركيز ١٠ ميكروجرام من أحد الكونات المراد قياسهاأو أختيار تركيز متوسط مابين أعلي تركيز وأقل تركيز للمحاليل القياسية العيارية. ويجب أن يكون متوسط النتائج ± ٢٠% من التركيز الأصلي.**

تابع التقيم المبدئي للمختبر
Initial Demonstration of Capability (IDC)

التقيم الاولي للدقة: Initial Demonstration of Accuracy

- من النتائج المتحصل عليها في الفقرة السابقة يتم حساب متوسط معدل الأنحراف(SD) Standard Deviation لجميع النتائج والفرق في معدل ألنحراف مابين تركزين وعلي هذا الأساس يحسب معدل أنحراف النسبي ويشترط الايزيد عن ٢٥ %. يمكن تحليل عدد عينتيان معملية معلومة التركيز والقيام بنفس الحسابات.

$$\% \text{ RSD} = \frac{(SD1-SD2) \times 100}{\text{SD average}}$$

تابع التقيم المبدئي للمختبر
Initial Demonstration of Capability (IDC)

تعين حد التقدير: Detection Limit (DL)

- يتم حسابة حد التقدير لكل عنصر كالاتى:
- The DL for ech metal is calculated as DL= 3 x standard deviation of the mean of the blank determinations (n > 20).
- ويعتبر حد التقدير غير ثابت حيث انة يحتاج الى إعادة تقيم من وقت لاخر تبعا للتغير فى مستوى الضابط المعملى (Blank)

التحقق من جودة ودقة النتائج

- ضابط الكواشف المعملية:Laboratory Reagent Blank
- يتم القيام بتحليل عينة ضابط كواشف معملية مع كل حزمة التحاليل Analysis Batch وذلك للتأكد من خلو ها من أي شوائب أو للتعرف علي التركيز الموجودBack ground concentration نتيجة استخدام هذه الكواشف.
- اختبار المعايرة المستمر : Continuing Calibration Check (CCC)

Seite 209

تابع التحقق من جودة ودقة النتائج

- يتم بتحليل محلول قياسي عياري مع كل ٢٠ عينة Analysis Batch بحيث يكون تركيزه يقع بمتوسط أقل تركيز وأعلي تركيز.
- إختبار الجودة بإستخدام محلول قياسي بديل Surrogate Standard (SUR) .
- يتم أضافة تركيز معين من المحلول القياسي البديل SURالي العينة ومن نتائج التحليل يمكن تحديد الجودة

Seite 210

تابع التحقق من جودة ودقة النتائج

ضابط معملي مذدوج للتحقق من صحة النتائج وجودتها: (LFSMD)

- تقسم عينة حقلية مضاف اليها المكونات المراد قياسها الي قسمين متساوين تماما، ويتم تحليلهما مع كل ٢٠ عينة (Batch Analysis) تحت نفس الظروف وبنفس الطريقة والمواصفات ومن نتائج التحاليل يمكن التأكد من صحة النتائج وذلك بحساب الفرق النسبي بين النتيجتين.
- يمكن حساب الفرق النسبي بتحليل عينتان حقليتنان من نفس الموقع وتحت نفس ظرف جمع العينات والتحاليل .

تابع التحقق من جودة ودقة النتائج

- **عينة مرجعية للتحقق من صحة النتائج:**
  Quality Control Sample (QCS)

تحضر في المعمل من المحاليل القياسية الأولية ويمكن الحصول عليها من جهات معتمدة ويتم تحليلها ومن نتائج التحاليل يمكن حساب صحة وجودة النتائج لكل عنصر ويشترط أن تكون في حدود± ٢٥ %.

المعايرة: Calibration

- **المحاليل القياسية العيارية**

تحضر المحاليل القياسية العيارية عند تراكيز مختلفة لاتقل عن خمشة تراكيز ، وذلك بإضافة حجم معين من Stock standard solution 1000 mg/L الي قارورة عيارية سعة ١٠٠ مل تحتوي علي حمض مخفف مناسب (حمض نيتريك أو حمض هيدروكلوريك المخفف)، METB ثم التخفيف الي ١٠٠ مل.

- **المحلول العيارى الوسط: (Intermediate standard solution (A)(100 mg/ml**

يتم ذلك بتخفيف ١٠مل من المحلول المركزة (Stock standard solution 1000 mg/L) وبنقل الى قارورة عيارية سعة ١٠٠ مل تحتوي علي الحمض المخفف المناسب ثم التخفيف الي ١٠٠ مل.

- **المحلول العيارى الوسط (ب)(Intermediate (mg/ml 10 standard solution (B)**

- **يتم ذلك بتخفيف ١٠ مل من المحلول Intermediate standard solution (A)(100 mg/ml) الي قارورة عيارية سعة ١٠٠مل تحتوي علي الحمض المخفف المناسب ثم التخفيف الي ١٠٠ مل.**

- **المحلول العيارى الوسط (ج) (Intermediate (mg/ml 10 standard solution (C)**

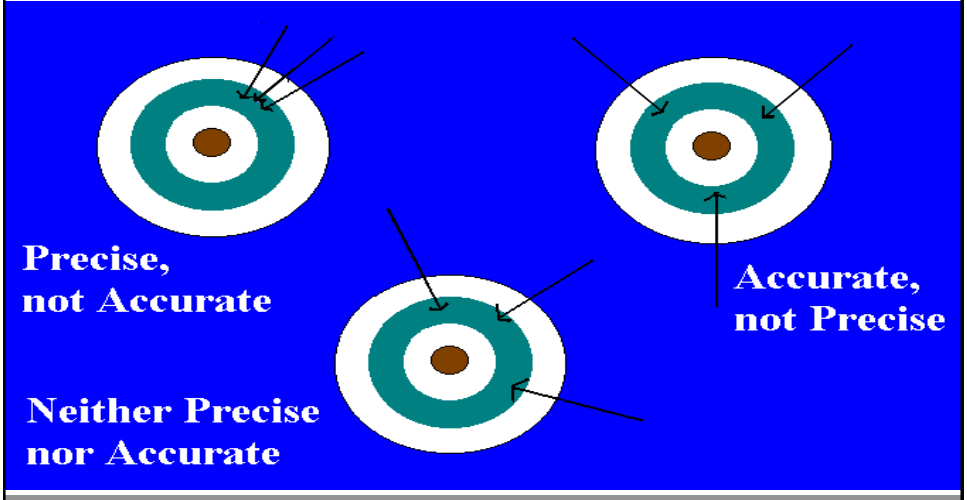
- **يتم ذلك بتخفيف ١٠ مل من المحلول Intermediate standard solution (B)(10 mg/ml) الي قارورة عيارية سعة ١٠٠مل تحتوي علي الحمض المخفف المناسب ثم التخفيف الي ١٠٠ مل.**

تابع التحقق من جودة ودقة النتائج

- **محاليل العمل القياسية: Working standard solution**

يتم تخفيف أحجام مختلفة من المحلول العيارى الوسط (ج) (١ mg/ml) الى قارورة عيارية سعة ١٠٠ مل ثم التخفيف الي ١٠٠ مل بحمض مخفف مناسب (حمض نيتريك أو حمض هيدروكلوريك المخفف) للحصول على تركيزات مختلفة لعمل المنحنى العيارى للعنصر المراد تقديرة.

تابع التقيم المبدئي للمختبر
Initial Demonstration of Capability (IDC)



تثبيت طريقة التحليل

Validation of analytical method

- **التثبت Validation:**

تأكيد صحة القياس عن طريق الاختبار وتقديم أدلة موضوعية على أن متطلبات محددة قد تم تحقيقها

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التثبت من صحة الطريقة Method Validation:

- عمـلية تبـرهـن خـــواص الأداء ومحـددات استخدام الطريقـة كما تعرف المؤثرات التي قـد تغيـر هـذه الخـواص وإلـى أي مـــدى بالإضـافـة إلى تحـديـد المقيـس أو الخـواص المقيسة داخل منظـومة في وجـود التداخـلات والمؤثـرات المحتمـلة. كما تبيـن درجـة صحـة النتائــج ودقتها التي يمكـن للطريقـة تحقيقهـا في إطــار ظروف خـواص الأداء والمحـــددات والمؤثرات.
- عملية تؤكد صلاحية الطريقة للغرض منها أي ملاءمتها لحل مشكلة معينة.

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متى يجـب التـثبـت ؟

- عند إصدار طريقة جديدة لمعالجة مشكلة محددة.
- مراجعة طريقة تستخدم لتحسينها أو لتعالج مشكلة إضافية.
- إذا أظهرت إجراءات ضبط الجودة أن نتائج طريقة مستخدمة تتأثر بالوقت.
- عند استخدام الطريقة في معمل مختلف أو بواسطة أفراد آخرين أو باستخدام أجهزة مختلفة.
- لبيان تكافؤ طريقتان مثل طريقة جديدة ومواصفة قياسية للاختبار.

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أ) كيفية إختيار طرق التحليل:

- ملائمة للاختيار/المعايرة المطلوبة
- يفضل ان تكون منشورة في مواصفة دولية أو إقليمية أو وطنية
- أحدث الإصدارات السارية للمواصفة ما لم يكن ذلك غير مناسب أو غير ممكن.
- يمكن استخدام طرق طورها المعمل أو طرق يتبناها المعمل شريطة أن تكون مناسبة للغرض وتم التحقق من صحتها.
- فى حالة إستخدام طرق غير قياسية يجب التحقق من صحة الطريقة بالشكل المناسب قبل استخدامه.

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وضع إجراءات طرق الاختبار أو المعايرة الجديدة قبل إجراء الاختبارات و/أو المعايرات حيث تحتوى هذه الطرق على المعلومات التالية على الأقل:

أ تعريف مناسب للطريقة و مجال عملها

ب وصف لطراز الغرض المراد اختباره أو معايرته

ج العناصر والكميات والمدى المراد تحديدها

د الأجهزة المستخدمة ومتطلبات الأداء الفني و مرجع القياس

هـ الظروف البيئية المطلوبة.

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و وصف للطريقة يتضمن :

- المراجعات اللازمة قبل بدء العمل
- التحقق من أن المعدة تعمل بشكل صحيح قبل كل استخدام.
- طريقة تسجيل القراءات والنتائج
- أي إجراءات لضمان السلامة يجب مراعاتها.
- المقومات و/أو متطلبات القبول أو الرفض
- البيانات الواجب تسجيلها وطرق التحليل وعرض النتائج.
- اللايقين أو طريقة تقدير اللايقين.
- وضع علامات تمييز الغرض وتناوله ونقله وتخزينه وإعداده للقياس.

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كيفية التحقق من صحة الطرق:

1. التحقق من صحة الطريقة هو التأكد بالفحص وتقديم الأدلة الموضوعية على أن الاحتياجات المعنية لتحقيق غرض محدد قد تم توفرها.

2. على المعمل أن يتحقق من صحة الطرق الغير قياسية والطرق التي تم تصميمها / تطويرها بواسطة المعمل والطرق القياسية المستخدمة خارج المجال المراد لها والإسهاب أو التوسع والتعديلات التي قد يدخلها على الطرق القياسية وذلك للتأكد من صلاحية الطرق للغرض المقصود هذا ويلزم أن يكون التحقق شاملاً حسبما يجب لمواجهة احتياجات التطبيق ومجالاته.

وعلى المعمل أن يسجل النتائج المستخرجة والطريقة المستخدمة للتحقق ونص يوضح ما إذا كانت الطريقة صالحة للغرض المقصود.

3. يلزم أن يكون المدى وصحة القيم التي يحصل عليها المعمل من الطرق المحقق صحتها وثيق الصلة باحتياجات الزبون للغرض المستخدمة من أجله هذه الطرق.

ومن أمثلة المدى والقيم: قيمة اللايقين uncertainity في نتائج القياس وحدود الكشف وخطية النتائج وحدود التكرارية و/أو تطابق استخراجية النتائج وثباتها أمام المؤثرات الخارجية.

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تقدير قيمة اللايقين في نتائج القياس:

- يجب تقدير قيمة اللايقين في نتائج القياس بشكل يمكن فهمه ويسهل استخدامه. يمكن الحصول على أغلب المعلومات المطلوبة لتقدير اللايقين أثناء إجراء عملية التثبت من صحة طرق القياس

- على معمل المعايرة أو معمل الاختبار الذي يجري المعايرات المراجعة الخاصة به أن يطبق طريقة لتقدير اللايقين في نتائج القياس لكل المعايرات

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- في حالات معينة تحول طبيعة طريقة الاختبار دون إجراء حسابات بالغة الدقة وصحيحة لقيم اللايقين في نتائج القياس يتعين على المعمل – على أقل تقدير – محاولة تعيين كل مكونات اللايقين وعمل تقدير معقول لقيمها.

- عند تقدير قيمة اللايقين في نتائج القياس يلزم أخذ كل مكونات اللايقين الهامة للحالة موضع الاعتبار مع استخدام طرق التحليل المناسبة.

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عناصر التثبت والمصطلحات

- **الاختبـــار Test:**

عملية فنية تنتهي بتحديد خاصية أو أكثر لمنتج معين طبقا لطريقة محددة

- **معمل اختبـــار Test Laboratory:**

المعمل الذي يؤدي اختبارات ويمكن أن يكون المعمل كيان قانوني أو كيان فني أو كلاهما.

- **الغرض المختبر Test Item:**

المادة أو المنتج المقدم للمعمل بغرض استخدامه في اختبارات الكفاءة الفنية.

- **طريقة الاختبـــار Test Method:**

طريقة فنية محددة لأداء الاختبار

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- **نتيجة الاختبـــار Test Result:**

قيمة خاصية تم تعيينها بالكامل عن طريق طريقة قياس محددة

- **صحة (جهاز قياس) Accuracy:**

قدرة جهاز القياس لإعطاء استجابة قريبة من القيمة الحقيقية

- **القيمـــة:**

- **القيمة الحقيقية True Value:**

قيمة متوافقة مع تعريف كمية معينة (غير معروفة بالطبيعة).

- **القيمة الحقيقية المتفق عليها:**

Conventional True Value (Assigned Value)

- قيمة تنسب لكمية معينة وتقبل – أحيانا عرفيا – بقيمة لايقين مناسب لغرض معين.
- **القيمة المرجعية المقبولة :**

Accepted Reference Value:

- القيمة المتفق على أن تمثل قيمة مرجعية للمقارنة وتشتق على أساس:
  - » مبادئ نظرية أو علمية
  - » قيمة موثقة من عمل معملي قومي أو منظمة دولية
  - » قيمة مجمع عليها نتيجة عمل معملي تعاوني
- قيمة متوسطة لمجموعة محددة من القياسات

- **اختبار كفاءة (المعمل)**

- **(Laboratory) proficiency testing:**

تقييم أداء المعمل في الاختبارات عن طريق المقارنات بين المعملية.

- **المقارنات بين المعملية**

- **Interlaboratory comparisons:**

عملية تنظيم وأداء وتقييم اختبارات تجرى على نفس الغرض المختبر أو مثيله بواسطة معملين أو أكثر طبقا لشروط محددة مسبقا.

في بعض الحالات قد يكون أحد المعامل المشاركة في برنامج المقارنات بين المعملية هو المعمل الذي يقدم القيمة الحقيقية المتفق عليها للغرض موضع الاختبار.

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- **مادة مرجعية :Reference material [RM]**

مادة ذات خاصية أو خواص متجانسة بشكل كافي ومثبتة بشكل جيد لتستخدم في معايـــرة جهـــاز أو تقييـــم طريقـــة قيـــاس أو إعطاء قيمة متفق عليها لخواص المواد.

- **مادة مرجعية موثقة**

- **Certified reference material (CRM):**

مادة مرجعية مصحوبة بشهادة توثق قيمة خاصية أو خواص بطريقة تثبت الإسناد إلى تحقيق صحيح للوحدة التي يعبر عن الخاصية بها ويصاحب قيمة كل خاصية قيمة للايقين محددة بدرجة ثقة محددة.

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- **معمل مرجعي :Reference laboratory**

المعمل الذي يقدم القيم المرجعية للغرض المراد اختباره (مثال: معهد معايرة قومي)

- **التتبعيـــة :Traceability**

خاصيـــة نتيجـة قيـــاس أو قيمـة قيـاسيـــة يمـكن نسبهـا وإسنادها إلى قيمة مرجعية مقررة ـ عادة ماتكون قومية أو دولية – من خلال سلسلة متصلة من المقارنـــات ذات النتائج المصحوبة بقيم لايقين.

- **قوة (الطريقة): Robustness**

قوة الطريقة التحليلية هي مقياس لقدرتها على البقـاء دون التأثر بالتغيرات الصغيـرة المتعمـدة في عناصر الطريقة وتبين معولية استخدامها في الظروف المعتادة.

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- **اختبار معولية (الطريقة): Ruggedness Test:**
- دراسة معمليـــة لبحث سير عمليـــة تحليليـــة عند إحداث تغيـرات صغيرة في الظروف البيئية و/أو ظروف التشغيل مماثلـة لما قد يحدث في ظروف مختلفة للاختبار. ويتيح اختبـار المعوليـة الحصـــول السريـــع والمنهجي على معلومـات عن تأثيـر التغيرات البسيطة.
- **القيمة البعيدة : Outlier**
- قيمـة غير متوافقـة مع بـاقي القيم المنتميـة إلى نفس المجموعة
- **نتيجة متطرفة: Extreme results**
- القيم البعيدة والقيم الأخرى الغير متوافقـة بشكل كبير مع القيم الأخرى المنتمية لنفس مجموعة البيانات. وقد يكـون لهـذه النتائـج تأثيرا عميقـا على الخـواص الإحصائية مثل المتوسط الحسابي والانحراف المعياري.

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- **التقنيات الإحصائية الفعالة:**
- **Robust statistical techniques**

تقنيات لتقليل تأثير النتائج المتطرفة على تقديـر قيـم المتوسـط الحسـابي والإنحـراف المعيـاري. وتستخدم هذه الأساليب لتقليـل وزن النتائـج المتطرفة بدلا من حذف هذه النتائج من مجموعة البيانات.

- **التكـراريـة : Repeatability**

هى الدقـة تحت ظـروف متكـررة ، بمعنى الظروف التي يمكن أن تعطى نتائج اختبار مستقل باستخدام نفس الطريقة على غرض مراد اختباره مماثل تماما في نفس المعمل بواسطة نفس الشخص مستخـدما نفس الأدوات خلال فترة زمنية قصيرة.

- **تكـراريــة (نتائج القياس) : Repeatability**

مدى قرب الاتفاق بين نتائج عمليات قياس متتابعة لنفس المقيس تمت تحت نفس ظروف القياس.

- **تكـراريــة (جهاز القياس) : Repeatability**

قدرة جهاز القيــاس على إعطاء نتائج متماثلة عند تكرار قياس نفس المقيس تحت نفس ظروف القياس.

- **تكـراريــة النتاج: Reproducibility**

هى الدقة تحت ظروف إنتــاج متكررة، بمعنى الظـروف التي يمكن أن تعطى نتائج اختبار باستخدام نفس الطريقة على غرض مراد اختباره مماثل تماما في معامل مختلفة بواسطة أشخاص مختلفين باستخدام أدوات مختلفة. ويلاحـظ أن النص الدال على تكـرارية النتـاج يجب أن يتضمن تحديد الظروف التي تغيرت.

- **اللايقين فى القياس:**

Uncertainty of measurement

هو قيمة مرتبطة بنتيجة القياس تحدد مدى تشتت القيم التي يمكن أن تميز أو تنسب إلى المقيس.

- **اللايقين المعيارى:**

Standard Uncertainty u(xi)

اللايقين في نتيجة قياس معبر عنه بقيمة انحراف معياري واحد.

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▪ اللايقين المعياري المجمع:

Combined Standard Uncertainty uc(y):

اللايقين المعياري لنتيجة القياس عندما نحصل على النتيجة من قيم لعدد من الكميات ، وتساوي القيمة الموجبة للجذر التربيعي لمجموع مربعات أطراف حيث يعرف الطرف بأنه قيمة تعبر عن تفاوت أو اختلاف قيم هذه الكميات بعد تحديد ثقل تأثير هذه الكميات على تغيرنتيجة القياس تبعا لهذه الكميات.

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▪ اللايقين الموسع: Expanded Uncertainty U

هو كمية تحدد مدى لنتيجة قياس يتوقع أن يحصر نسبة كبيرة من توزيع القيم التي يمكن نسبتها للمقيس.

▪ معامل التغطية أو الامتداد: Coverage factor k

هو معامل عددي يستخدم لمضاعفة قيمة اللايقين المعياري المجمع للحصول على قيمة اللايقين الموسع. وعادة ما تكون قيمة هذا المعامل بين ٢ و ٣.

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- **اختبارات الكفاءة Proficiency testing (PT)**
- **اختبار الكفاءة (للمعمل)**

(Laboratory) proficiency testing:

هو قياس لكفاءة أداء المعمل من خلال المقارنات البين معملية (دليل الأيزو ٢)

- **المقارنات البين معملية:Interlaboratory comparisons**

عملية تنظيم وأداء وتقييم اختبارات على نفس الغرض أو مثيله تتم فب معملين أو أكثر طبقا لشروط موضوعة مسبقا.

مع ملاحظة أنه في بعض الحـالات يكـون أحد المعامل هو المعمل الذي يعطي القيمة الحقيقيـة المتفق عليها للغرض أو الخاصية تحت الاختبار

assigned value for the test item

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أدوات التحقـق

1- اختبارات الكفاءة بنظام القياس المقارن:

PT Measurement comparison schemes:

يتضمن هذا النظام تمرير الغرض المراد اختباره من معمل للمعمل التالي على التتابع

2- اختبارات الكفاءة بنظام المقارنات البين معملية:

PT Interlaboratory testing schemes:

يتضمن هذا النظام توزيع عشوائي متزامن لعينات فرعية من عينة واحدة على المعامل المشاركة للاختبار المتزامن.

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3- اختبارات الكفاءة بنظام العينات المجزأة

PT Split-sample testing schemes:

يتضمن هذا النظام مقارنة بيانات عدد صغير من المعامل (غالبا معملين) تحت التقييم كمعامل تقدم خدمة الاختبار.

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4- اختبارات الكفاءة الوصفية

PT Qualitative schemes:

تقييم أداء معمل اختبار وقدراته على توصيف وجود أو كائن معين مثل توصيف نوع الأسبستس أو توصيف كائن حى مسبب للمرض ولهذا يكتسب نظام اختبار الكفاءة الصفة الوصفية.

5- اختبارات الكفاءة بنظام القيمة المعلومة

PT Known – value schemes:

تتضمن بعض نظم اختبارات الكفاءة إعداد أغراض للاختبار ذات قيمة معلومة للمقيس ومن ثم يمكن تقييم قدرة معمل ما على اختبار غرض ومقارنة نتائجه بالقيمة الحقيقية المتفق عليها. هذا النوع من اختبارات الكفاءة لايتطلب اشتراك عدد كبير من المعامل.

6- اختبارات الكفاءة بنظام العمليات الجزئية:

PT Partial-process schemes:

تتضمن هذه النوعية الخاصة من نظم اختبارات الكفاءة تقييم قدرة المعامل على أداء جـزء من اختبــار شـامل أو عملية قياس كلية.

أمثلة:

- لمعامل التي تقـوم بتحليـل وتحويـل
- البيانات وتصدر تقرير بدلا من إجراء
- الاختبار أو القياس الفعلي .
- المعامل التي تعد العينات طبقا لمواصفات محددة.

تحليل النتـــائج

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- **الهـدف:**

تهدف عمليات تحليل ومقارنات نتائج القياس إلى:

- التعرف على مدى دقة القياس في كل معمل من المعامل التي يشملها النظام القومي للقياس خاصة تلك التي تطلب اعتماد معاملها وتقييمها بين الحين والآخر
- تعيين قيمة ثابت فيزيائي من نتائج مجموعة من المعامل
- مقارنة القيم المتوسطة لمجموعة من التجارب بقيمة عيارية أخرى
- الاعتراف المنهجي بكفاءة المعمل في إجراء اختبار / معايرة في نشاط معين .. في مدى قياس محدد . بدرجة دقة معروفة . بمستوى ثقة معلن طبقا للمواصفات الدولية . يظل هو الهدف البارز.

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- **الطـــرق:**
- أكثر الطرق شيوعا واستخداما في علم المترولوجيا للمقارنة بين النتائج الواردة من معامل مختلفة وطرق مختلفة لنفس المقيس:
  - الطريقة الأولى (ANOVA)
  - الطريقة الثانية (اختبار فيشر)
  - الطريقة الثالثة (اختبار الكفاءة)
  - الطريقة الرابعة (منهجية الاستبعاد)
  - الطريقة الخامسة (X-Bar Chart)
  - الطريقة السادسة (مخططات التحكم)
  - الطريقة السابعة (المقارنة المباشرة للنتائج).

الطريقة الأولى ANOVA

- إحدى الطرق الإحصائية التي تهدف إلى مقارنة كل من النتيجة (المقاسة) و النتيجة (العيارية) والحكم عليهما هل هما (متوافقان معا .. أم غير متوافقين معا) بمعنى آخر إثبات مدى تشابه النتيجتين من عدمه.

- ضرورة أن تكون جميع النتائج المسجلة بالمعمل في نفس الظروف البيئية والمعملية و التجهيزية قدر الإمكان تجنبا لوجود مصادر الخطأ الرتيب.

الطريقة الثانية – إختبار فيشر F- Test

- تهدف الطريقة بشكل أساسي إلى مقارنة طريقتين للقياس ببعضهما . الأولى الطريقة تحت التحقق و التقييم والثانية التي أجريت بمعمل عياري مرجعي لتحديد قيمة نفس المقيس.

- تجيب هذه الطريقة على السؤال:. هل الطريقتان متماثلتان ولهما نفس الدقة؟

الطريقة الثالثة – إختبار الكفاءة

- إجراء اختبار الكفاءة للمعامل لتحديد مدى إمكانية اعتماده في قيمة محددة و مقاسة
- تفيد هذه الطريقة المعامل التي ترغب في اعتمادها دوليا عند قيمة مقاسة معينة أو المعمل الذي قد تم اعتماده بالفعل مسبقا لكن يراد إجراء متابعة له للتأكد من استمرارية تحقيقه لمبدأ الاعتماد.

- لاتتطلب الطريقة عمليات إحصائية معقدة أو رسومات بيانية وخلافه إنما تتطلب فقط :
  - معرفة القيمة المقاسة في كل من المعمل الذي يطلب الاعتماد و المعمل العياري المرجعي
  - معرفة قيمة اللايقين المحسوبة في كل من المعملين.
  - استخدام معادلة رياضية بسيطة يتم بعدها تقرير ما إذا كان يمكن اعتماد هذا المعمل في نقطة القياس هذه أم لا !! كما يمكن بعدها الحكم على نجاح اختبار الكفاءة للقيمة المقاسة من عدمه

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خطوات إجراء اختبار الكفاءة

- يتم تحديد كل من مقدار القيمة المقاسة Rv و اللايقين في قياسها URV±بوحدات الـ ppm
- يقوم المعمل المطلوب عمل اختبار الكفاءة له بإجراء القياس عند نفس القيم المحددة سلفا بالبروتوكول حيث يتم تعيين مقدار القيمة المقاسة LV و قيمة اللايقين في قياسها ULv ± بوحدات الـ ppm أيضا

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- يتم التقييم لكل قيمة مقاسة بحساب ما يعرف بـ En Ratio عند هذه القيمة من العلاقة التالية :
- $En = LV - Rv / \sqrt{ULv2 + URV2}$
- ـ يجب أن تكون قيمة En المحسوبة من المعادلة أقل من الواحد الصحيح حتى يمكن اعتماد المعمل عند هذه القيمة .. فإذا زادت قيمة En عن الواحد الصحيح فسوف يلزم استبعاد هذه القيمة المقاسة من جدول اعتماد المعمل

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الطريقة الرابعة - (منهجية الاستبعاد)

- تهدف هذه الطريقة إلى استبعاد القراءة الشاذة والمتطرفة أو تلك شديدة التباعد عن باقي القراءات المأخوذة لنفس المقيس في نفس الظروف ..
- عند تسجيل عدد كبير من النتائج عند تكرار التجربة لمقيس واحد في نفس الظروف فقد تظهر نتيجة أو أكثر من نتيجة شديدة التباعد عن باقي النتائج
- يتم هذا الاستبعاد بعد إجراء عملية إحصائية معينة يتم بعدها اتخاذ القرار المناسب تجاه هذه النتيجة.

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خطوات الطريقة ..

- يتم تسجيل عدد n من النتائج على المقيس الواحد وفي نفس ظروف التجربة بحيث لا يكون هناك شك في إحدى النتائج المأخوذة
- قد تكون أصغر النتائج هي شديدة التباعد عن باقي المجموعة و مشكوك فيها ..هنا نرتب النتائج ترتيبا تصاعديا من الأصغر إلى الأكبر (X1 < X2 < X3 <..... < Xn)
- أو قد تكون أكبر النتائج هي شديدة التباعد عن باقي المجموعة ومشكوك فيها .. هنا نرتب النتائج ترتيبا تنازليا من الأكبر إلى الأصغر (X1 > X2 > X3 > ..... > Xn)

- هب أننا بصدد الاحتمال الأول كما في الخطوة ٢ ، وأن عدد النتائج المأخوذة يقع بين ٣ الى ٧ قراءات ..نحسب قيمة المدى بين أصغر قيمة و القيمة التالية لها و لتكن X2 – X1 ثم نحسب المدى بين أصغر قيمة و أكبر قيمة (أي خلال المدى بالكامل) و لتكن Xn – X1
- نحسب النسبة بين المقدارين السابقين (r10) كما يلي:

$$r10 = (X2 - X1) / (Xn - X1)$$

- نقارن الآن بين قيمة r10 المحسوبة من العلاقة السابقة وبين قيمتها من الجدول وعند درجة معنوية ٥% (مستوى ثقة ٩٥%) أو عند درجة معنوية ١ % (مستوى ثقة ٩٩%) فإذا كانت القيمة المحسوبة من العلاقة أكبر من القيمة الموجودة بالجدول فإنه من الأفضل استبعاد هذه النتيجة

الطريقة الخامسة - X – Bar Chart

- أسلوب بياني إحصائي للحكم على أداء النتائج المأخوذة بأنه تحت السيطرة و التحكم
- تهدف إلى الحكم على عملية قياس معينة من حيث كونها تحت التحكم والسيطرة.
- اختبار ما يعرف بـ (مدى الاستقرارية) لنتيجة قياس معين.
- من أمثلة تطبيق هذه الطريقة معايرة جهاز مرجعي أو قيمة عيارية تتم دوريا خلال مدى عريض من الزمن قد يصل إلى عام كامل. كذلك يمكن تطبيقها على نتيجة متوسطة مأخوذة من عدد كبير من النتائج بحيث يتكرر أخذ هذه القيمة المتوسطة مرات ومرات خلال فترة زمنية طويلة
- يعتد بها كعنصر أساسي من عناصر طرق توكيد.

الطريقة السـادســـة – مخططات التحكم Control Charts

- طريقة إحصائية بيانية لضبط وتوكيد صحة القياس.
- أسلوب تخطيطي للحكم على أداء عمليات القياس إذا كان في حالة التحكم والسيطرة الإحصائية من عدمه.
- تفيد في حالات مقارنة التغيرات الحادثة في قيمة عيارية بحدود التحكم المسموح بها لهذه القيمة.
- الدور الرئيسي لهذه المخططات هو حساب تلك الحدود التي يجب أن تقع خلالها قيمة قياسية معينة حتى نحكم عليها أنها في حالة الاستقرار الإحصائي و أن التغيرات التي يمكن أن تحدث بها في نطاق الموافقة والقبول.

الطريقة السـابعـة – المقارنة المباشرة للنتائج

تهدف الطريقة إلى إجراء مقارنة سريعة وبسيطة لنتائج المعامل المشاركة في حلقة قياس مغلقة حول قيمة عيارية معينة بحيث تشمل هذه المقارنة السريعة مقارنة كل من القيم المتوسطة للنتائج وكذلك اللايقين المصاحب لهذه القيمة المتوسطة وذلك من خلال مخطط بياني بسيط

Validation of analytical procedures

Contents

Validation of analytical procedures

Validation is the process of determining of the performance characteristics of the method/procedure or process.

Two main types of validation may be distinguished:

- **Validation of standard procedures.**
- **(Accepted by national or international standardization organization)**
- **Validation of own procedures.**
- **The in-house validation of methods or procedures by individual user-laboratories.**

To specify the performance of procedure, a selection of the following basic parameter is determined:

- **Trueness (accuracy), bias**
- **Trueness (accuracy), bias.**
- **Recovery**
- **Sensitivity**
- **Specify and selectivity**
- **Working range (including MDL)**
- **Interference**
- **Ruggedness or robustness.**

1- Trueness (accuracy), bias:

- **To know about a method is whether the results reflect the true value for the analyte or property. And if not, can the (un) trueness or bias be quantified and possibly corrected.**
  - **The direct method is by carrying out replicate analyses (n> 10) with the method on a certified reference sample with a known content of the analyte.**

- **The indirect method by comparing the results of the method with those of a reference method or accepted method) both applied to same sample(s).**
- **To verify bias is by having (some) samples analyzed by another laboratory and by participation in inter- laboratory exchange programs.**

2.Precision:

- Replicate analyses performed on a reference sample yielding a mean to determine trueness or bias.
- Also, yield a standard deviation of the mean as a measure for precision.

- F- test can be used for the comparison between the obtained standard deviation and with the standard deviation given for the reference sample.
- Numerically, precision is either expressed by the absolute value of the standard deviation or, more universally, by the relative standard deviation (RSD) or coefficient of variation (CV).

- **2.1. Reproducibility:**
  - **The absolute difference between two single test results obtained with the same test method on identical test material in different laboratories by different operators using different equipment will exceed the reproducibly limit R in not more than 5% of the cases.**

- **The measure of reproducibility R is the standard deviation of these results Standard for a not too small number of data ($n \geq 8$) R is defined by (95% confidence):**

$$R = 2\sqrt{2}\,x\,SR$$

- **2.2. Repeatability:**
  - **The absolute difference between two independent single test results obtained with the same test method identical test material in the same laboratory by the by the same operator using the same apparatus within the shortest time interval will exceed the repeatability limit (r) in not more than 5% of the cases.**

- **The measure for the repeatability r is the standard deviation of the results Sr, and for a not too small number of data (n ≥ 10) R is defined by (95% confidence):**

$$r = 2\sqrt{2} \times Sr$$

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3. Sensitivity:

- **This a measure for the response y of the instrument or of a whole method to the concentration C of the analyte or property, e.g. the slope of the analytical calibration graphs.**
- **The sensitivity of the analyte in the final sample extract may not necessary to equal to the sensitivity for the analyte in simple standard solution.**
- **Matrix effects may cause improper calibration of the measuring step of the analytical method**

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- **The sensitivity may not to be constant over a long range. It usually decreases at higher concentrations by saturation of the signal. This limits are the working range .**

4. Working range:

Determine the upper limit of the working range (the lower limit of a working range corresponds with the Method Detection Limit).

- **To determine the measuring range of solutions the following procedure can be applied:**
- **Prepare a standard solution of the analyte in the relevant matrix (e.g. extractant) at concentration beyond the highest expected concentration.**
- **Measure this solution and determine the instrument response.**

- Dilute this standard solution 10x with the matrix solution and measure again.
- Repeat dilution and measuring until the instrument gives no response.
- Plot the response (Absorbance) vs. the concentration.
- Estimate the useful part of the response graph.
- (If the dilution steps are too large to obtain reliable graph, they need to be reduced, e.g. 5x).

5. Recovery:

- To determine the effectiveness of the a method and also of the working range.
- Recovery can be defined as the fraction of the analyte determined after addition of a known amount of the analyte to sample.

- **Control samples are most commonly used for spiking.**
- **The sample as well as spikes are analyzed at least 10 times, the results averaged and the relative standard deviation (RSD calculated.**
- **The concentration level of the spikes depend on the purpose:**
  - **The level(s) will largely correspond with those of the test samples (recoveries at different levels may differ): A concentration midway the working range is a convenient choice.**
  - **For the determination of a working range a wide range may be necessary, at least to start with.**

Control chart:

- **Introduction:**

An internal system for quality control is needed to ensure that valid data continue to be produced.

This implies that systematic checks, .g. per day or per batch, must show that the test results remain reproducible and that the methodology is actually measuring the analyte each sample.

Types of control charts:

1. Control chart of the mean for the control of bias.
2. Control chart of the range of Duplicates for the control of precision.

1. Control Chart of the Mean (Mean Chart):

1.1. Principle:

- In each batch of test samples at least one conhtrol sample is analyzed.
- The results is plotted on the control chart of thre attribute and the control sample concerned

Control Chart of the Mean (Mean Chart):

- This chart shows the (assumed) relation with the normal distribution of the data around the mean.
- The basic assumption is that when a control result falls within a distance of (2 s) from the mean, the system was under control and the results of the batch as a whole can be accepted.

- **A control result beyond the distance of (2 s) from the mean (the warning limit) signals that may be wrong or tends to go wrong.**

- **While a control result beyond 3 S (the Control Limit or Action limit) indicates that the system was statistically out of control and the results have to be rejected: The batch has to be rejected sorting out what went wrong and after correcting the system.**
- **Control charts can be used for quite a number of other types of data that need to be controlled on a regular basis, e.g blanks, recoveries, standard deviations, instrument response.**

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