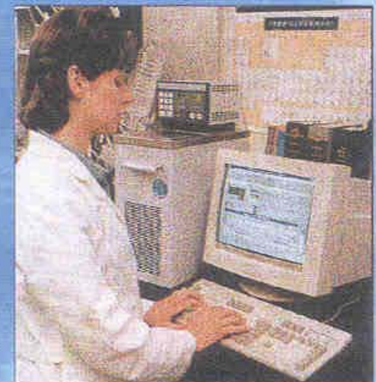
UN/ECE Task Force on Laboratory Quality Management & Accreditation

Sampling & Analytical Protocols

Laboratory Facilities

TECHNICAL REPORT: GUIDANCE TO OPERATION OF WATER QUALITY LABORATORIES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UN/ECE Task Force on
Laboratory Quality Management &
Accreditation

TECHNICAL REPORT: GUIDANCE TO OPERATION OF WATER QUALITY LABORATORIES

September 2002

PREFACE

The “Guidance to Operation of Water Quality Laboratories” was drawn up as part of the activity of the UN/ECE Task Force on Laboratory Quality Management & Accreditation (UN/ECE TF-LQM&A) under the Convention on the Protection and Use of Transboundary Watercourses and International Lakes (Helsinki, 1992) by taking into account the requirements of the Guidelines on Water-Quality Monitoring and Assessment of Transboundary Rivers (prepared by RIZA, the Netherlands as lead country of the UN-ECE Task Force on Monitoring and Assessment).

Before drawing-up the guidance the UN/ECE TF-LQM&A completed a survey on the present practices in the laboratories implementing water quality monitoring in the countries signatory to the Convention. The survey included: (a) information on the sampling and analytical methods used, (b) inventory on the laboratory facilities including instrumentation, and (c) the quality control measures and status of accreditation. 27 out of 46 countries responded to a Questionnaire, which had been distributed in English and Russian languages. In addition to the information from this survey, requirements of laboratory accreditation, guidelines for good laboratory practices, laboratory practices in developed countries and related documents (e.g., Handbook for Analytical Quality Control in Water and Wastewater Laboratories, US-EPA) have been taken into account during drawing-up the guidelines.

The guidance was revised by the members of the Task Force Core Group in December 1999, during the first half of 2000 and in the year 2001. It was discussed during the first and second meeting of Monitoring and Assessment Working Group too.

The guidance is addressed to laboratory managers, leaders of field investigations, and other personnel who bear responsibility for generation of water and wastewater data. Information is offered to assist the reader in establishment of water (environmental) laboratories, particularly taking into account the quality control measures needed for prevention and correction of factors leading to breakdowns in the validity of data.

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PART I.

1 INTRODUCTION

1.1 Objectives and Character of the Guidance

This guidance is intended to assist ECE Governments and joint bodies (e.g. bilateral or multilateral river commissions) in understanding laboratory quality management and providing guidance to laboratory managers to design or upgrade water laboratories and to strive for accreditation.

The target group comprises decision-makers in ministries with competence on environment, water management and human health; environmental, water, health and other competent agencies, and all those who are responsible for managing the monitoring and assessment of transboundary rivers.

The character of this guidance is technical rather than strategic as the latter aspects are being dealth with in the relevant chapters of the Guidelines on monitoring and assessment of transboundary rivers and transboundary groundwaters (see the documents for the forthcoming second meeting of the Parties to the Convention issued under symbol MP.WAT/2000/9 and 10).

1.2 Monitoring Cycle and Activities Dealt with in this Guidance

The process of monitoring and assessment should principally be seen as a sequence of related activities that starts with the definition of information needs, and ends with the use of the information product. This cycle of activities is shown in Figure 1.

Figure 1. The monitoring cycle

Successive activities in this monitoring cycle should be specified and designed based on the required information product as well as the preceding part of the chain. In drawing up programmes for the monitoring and assessment of river basins, riparian countries should jointly consider all stages of the monitoring process.

The guidelines on monitoring and assessment are supported with five background reports, which are as follows:

- Transboundary rivers and international lakes
- Current practices in monitoring and assessment of rivers and lakes
- Biological assessment methods for watercourses
- Quality assurance
- State of the art on monitoring and assessment of rivers

Although the guidelines and the background reports deals with some aspects of the laboratory work, particular the major quality assurance approaches, there is a need for guidance in establishment and upgrading laboratory work in water/environmental laboratories.

The evaluation of the obtained information may lead to new or redefined information needs, thus starting a new sequence of activities. In this way, the monitoring process will be improved.

The present guidance on laboratory quality management exclusively deals with the activity designated in the above figure by “Data collection”. This activity in the monitoring cycle is composed of a number of sub-activities such as collecting samples, ensuring quality work in laboratories and reporting analytical results.

The guidance summarised in the present document will address to laboratory managers designing or upgrading water laboratories and will help these laboratories in the countries in transition to be prepared for accreditation.

1.3 Laboratory Quality Management

Water quality targets, objectives and standards are set to evaluate the quality of the water resources, both surface and subsurface water bodies, to characterise ecological status (for surface waters) and to establish satisfactory condition for intended uses of the aquifer(s). The laboratory data define whether that condition is being met, and whether the water is at acceptable quality to fit for the purpose. If the laboratory results indicate a violation of the standard, action is required by the pollution control authorities. The analyst must be aware that his professional competence, the procedures he has used, and the reported values are reliable and may be used with confidence.

Similarly to the monitoring cycle in water management we can draw a measurement cycle for the implementation of the monitoring, starting with the collection of samples and closing with reporting the analytical results. As the place of the measurement cycle in the monitoring cycle is indicated in Figure 1 as “Data collection”, Figure 2 shows the

elements of the measurement cycle. It starts with the sampling and closes with reporting the measurement results.

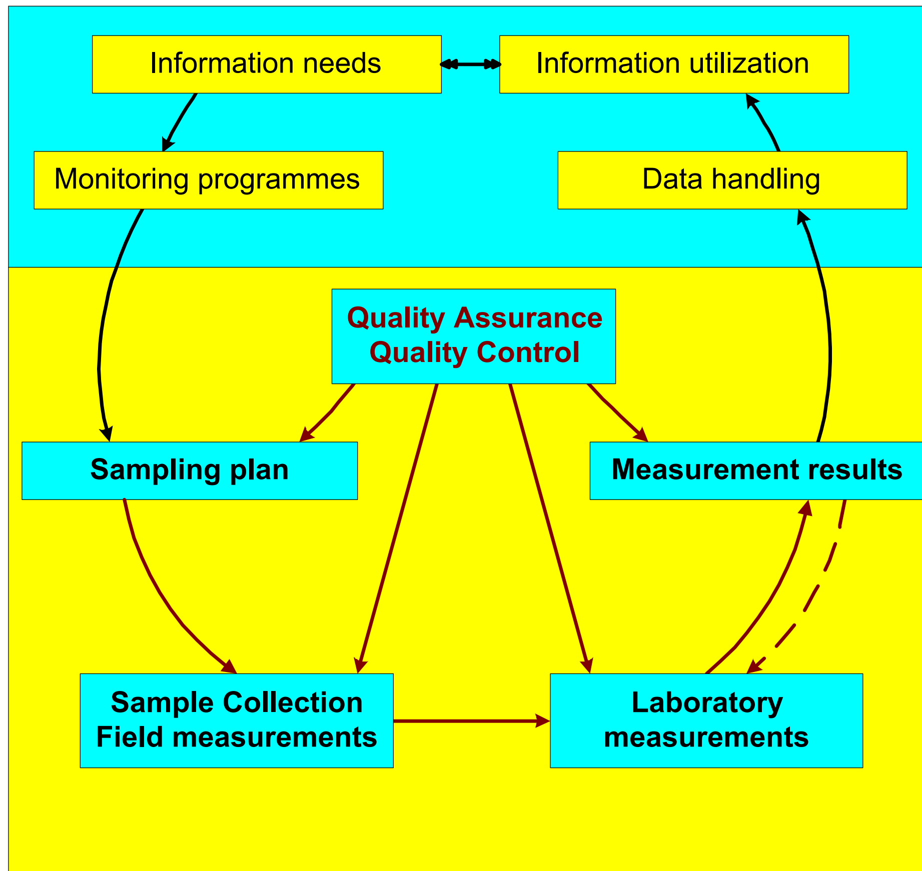

Figure 2. The measurement cycle ensuring the quality of the monitoring results.

Water quality monitoring rests upon a firm base of laboratory data. The role of the analytical laboratory is to provide the qualitative and quantitative data to be used for different purposes. The data must accurately describe the characteristics or the sample, or the type and concentration of constituents in the sample analysed in the laboratory. In many cases, an approximation or invalidated (incorrect) result is worse than no answer at all, because it will lead to miss interpretations.

The progress of research, effectiveness of pollution control will depend upon the validity of the results reported by the laboratory. Therefore, the laboratory data must be backed up by an adequate programme to document the proper control and application of all of the factors, which effect the final result.

Depending on the information needs of the water management, monitoring data collection relate to physical, chemical, radiological, hydrobiological, ecotoxicological and microbiological measurements. Generation of these data requires representative sampling followed by analytical work in specialised laboratories.

The design of the monitoring programme should describe the targeted water quality variables (characteristics, parameters, determinands), the matrices in the aquatic environment from where samples should be taken, analytical accuracy targets, including detection limits, application ranges and acceptable tolerances. The specialised laboratories should apply the appropriate sampling and analytical methods, should have the necessary rooms, should be properly equipped, having the necessary instrumentation. Skills of laboratory personnel must ensure the quality of the work during the sampling and the analyses.

Compilation of the guidance on laboratory quality management has been based on the expectation that sampling and laboratory work consider all kinds of measurements, which might be required during implementation of the water quality monitoring, detailed in the monitoring design. The guidance target considerations, which should taken during design and operation of the laboratories to generate reliable, comparable monitoring results.

The laboratory management should plan the work in the laboratory before starting with the sampling. Sampling and analytical methodologies must be defined as the first step of the implementation of the monitoring.

1.3.1 Methodologies

In general, the widespread use of a sampling or analytical method, its appearance in international/national methodological standard indicates that it is a reliable means of sampling or analysis. This fact tends to support the reliability of the results reported. The use of an individual method, or a little-known technique forces the data user to question the appropriateness and validity of the results.

The need for standardisation of methods or using standardised methods within a laboratory is readily apparent. Uniform methods among co-operating laboratories, e.g., implementing monitoring in international river basins, are also important in order to remove the methodology as a variable in comparison, or joint use of data. Uniformity of methods is particularly important when laboratories are providing data to a common data bank, or when several laboratories are co-operating in joint field surveys. The lack of standardisation of methods raises doubts as to the validity of the results reported. If the same constituent is measured by different analytical procedures within a single laboratory, or in several laboratories, the question is raised as to which procedure is superior, and why the superior method is not used.

Selection of an analytical method should be made by careful considerations. For example, physical and chemical methods for monitoring should be selected by the following criteria:

- The method should measure the desired constituent with precision and accuracy sufficient to meet the data needs even in the presence of interferences, which might be encountered in the samples. *Box 1 and Table 1 show the approach used in the Danube river basin transnational monitoring network.*

- The procedure should utilise the equipment and skills available in the laboratory.
- The selected methods should be in use that the methods are properly validated.
- The method should be sufficient to produce the measurement results within the required time-frame.

Box 1. Determinands: basis for selection of appropriate analytical method in the Danube river basin Tans-National Monitoring Network (TNMN)

The resulting lists of determinands for water and sediments as agreed for the Danube TNMN are presented in Table 1, together with the levels of interest and analytical accuracy targets, which are defined as follows:

- The minimum likely level of interest is the lowest concentration considered likely to be encountered or important in the TNMN.
- The principal level of interest is the concentration at which it is anticipated that most monitoring will be carried out.
- The required limit of detection is the target limit of detection (LOD), which laboratories are asked to achieve. This has been set, wherever practicable, at one third of the minimum level of interest. This is intended to ensure that the best possible precision is achieved at the principal level of interest and that relatively few "less than results" will be reported for samples at or near the lowest level of interest. Where the performance of current analyses is not likely to meet the criterion of a LOD of one third, if the lowest level of interest, the LOD has been revised to reflect best practice. In these cases, the targets have been entered in *italics*.
- The tolerance indicates the largest allowable analytical error which is consistent with the correct interpretation of the data and with current analytical practice. The target is expressed as “x concentration units or P%“. The larger of the two values applies for any given concentration. For example, if the target is 5 mg/l or 20% - at a concentration of 20 mg/l the maximum tolerable error is 5 mg/l (20% is 4 mg/l); at a concentration of 100 mg/l, the tolerable error is 20 mg/l (i.e. 20%) because this value exceeds the fixed target of 5 mg/l.
- Analytical accuracy targets for sediments are defined for <63 μm grain-size fraction.

Sediments comprise suspended solids and bottom sediments.

Table 1/a. Determinand list and accuracy targets for water in the Danube TNMN

Determinands in Water	Unit	Minimum likely level of interest	Principal level of interest	Target Limit of Detection	Tolerance
Flow	m^3/s	-	-	-	-
Temperature	°C	-	0-25	-	0.1
Suspended Solids	mg/l	1	10	*1*	*1 or 20%*
Dissolved Oxygen	mg/l	0.5	5	0.2	0.2 or 10%
pH	-	-	7.5	-	0.1
Conductivity @ 20 °C	µS/cm	30	300	5	5 or 10%
Alkalinity	mmol/l	1	10	0.1	0.1
Ammonium (NH_4^+ -N)	mg/l	0.05	0.5	0.02	0.02 or 20%
Nitrite (NO_2^- -N)	mg/l	0.005	0.02	*0.005*	*0.005 or 20%*
Nitrate (NO_3^- -N)	mg/l	0.2	1	0.1	0.1 or 20%
Organic Nitrogen	mg/l	0.2	2	0.1	0.1 or 20%
Orthophosphate (PO_4^{3-} -P)	mg/l	0.02	0.2	0.005	0.005 or 20%
Total Phosphorus	mg/l	0.05	0.5	0.01	0.01 or 20%
Sodium (Na^+)	mg/l	1	10	0.1	0.1 or 10%
Potassium (K^+)	mg/l	0.5	5	0.1	0.1 or 10%
Calcium (Ca^{2+})	mg/l	2	20	0.2	0.1 or 10%
Magnesium (Mg^{2+})	mg/l	0.5	5	0.1	0.2 or 10%
Chloride (Cl^-)	mg/l	5	50	1	1 or 10%
Sulphate (SO_4^{2-})	mg/l	5	50	5	5 or 20%
Iron (Fe)	mg/l	0.05	0.5	0.02	0.02 or 20%
Manganese (Mn)	mg/l	0.05	0.5	0.01	0.01 or 20%
Zinc (Zn)	µg/l	10	100	3	3 or 20%
Copper (Cu)	µg/l	10	100	3	3 or 20%
Chromium (Cr) - total	µg/l	10	100	3	3 or 20%
Lead (Pb)	µg/l	10	100	3	3 or 20%
Cadmium (Cd)	µg/l	1	10	*0.5*	*0.5 or 20%*
Mercury (Hg)	µg/l	0.2	2	0.1	0.1 or 20%
Nickel (Ni)	µg/l	10	100	3	3 or 20%
Arsenic (As)	µg/l	10	100	3	3 or 20%
Aluminium (Al)	µg/l	10	100	*10*	*10 or 20%*
BOD_5	mg/l	0.5	5	*0.5*	*0.5 or 20%*
COD_{Cr}	mg/l	10	50	*10*	*10 or 20%*
COD_{Mn}	mg/l	1	10	0.3	0.3 or 20%
DOC	mg/l	0.3	1	*0.3*	*0.3 or 20%*
Phenol index	mg/l	0.005	0.05	*0.005*	*0.005 or 30%*
Anionic active surfactants	mg/l	0.1	1	0.03	0.03 or 30%
Petroleum hydrocarbons	mg/l	0.05	0.2	*0.05*	*0.05 or 30%*
AOX	µg/l	10	100	10	10 or 20%
Lindane	µg/l	0.05	0.5	0.01	0.01 or 30%
pp'DDT	µg/l	0.05	0.5	0.01	0.01 or 30%
Atrazine	µg/l	0.1	1	0.02	0.02 or 30%
Chloroform	µg/l	0.1	1	0.02	0.02 or 30%
Carbon tetrachloride	µg/l	0.1	1	0.02	0.02 or 30%
Trichloroethylene	µg/l	0.1	1	0.02	0.02 or 30%
Tetrachloroethylene	µg/l	0.1	1	0.02	0.02 or 30%
Total Coliforms (37 C)	10^3 CFU/100 ml	-	-	-	-
Faecal Coliforms (44 C)	10^3 CFU/100 ml	-	-	-	-
Faecal Streptococci	10^3 CFU/100 ml	-	-	-	-
Salmonella sp.	in 1 litre	-	-	-	-
Macrozoobenthos	no. of taxa	-	-	-	-
Macrozoobenthos	Sapr. index	-	-	-	-
Chlorophyll – a	µg/l	-	-	-	-

Table 1/b. Determinand list and accuracy targets for sediments in the Danube TNMN

Determinands in sediments (dry matter)	Unit	Minimum likely level of interest	Principal level of interest	Target Limit of Detection	Tolerance
Organic Nitrogen	mg/kg	50	500	10	10 or 20%
Total Phosphorus	mg/kg	50	500	10	10 or 20%
Calcium (Ca^{2+})	mg/kg	1000	10000	300	300 or 20%
Magnesium (Mg^{2+})	mg/kg	1000	10000	300	300 or 20%
Iron (Fe)	mg/kg	50	500	20	20 or 20%
Manganese (Mn)	mg/kg	50	500	20	20 or 20%
Zinc (Zn)	mg/kg	250	500	50	50 or 20%
Copper (Cu)	mg/kg	2	20	*1*	*1 or 20%*
Chromium (Cr) – total	mg/kg	2	20	*1*	*1 or 20 %*
Lead (Pb)	mg/kg	2	20	*1*	*1 or 20 %*
Cadmium (Cd)	mg/kg	0.05	0.5	*0.05*	*0.05 or 20%*
Mercury (Hg)	mg/kg	0.05	0.5	0.01	0.01 or 20%
Nickel (Ni)	mg/kg	2	20	*1*	*1 or 20 %*
Arsenic (As)	mg/kg	2	20	*1*	*1 or 20 %*
Aluminium (Al)	mg/kg	50	500	*50*	*50 or 20%*
TOC	mg/kg	500	5000	100	100 or 20%
Petroleum hydrocarbons	mg/kg	10	100	1	1 or 30 %
Total solvent-extractable matter	mg/kg	100	1000	10	10 or 20 %
PAH – 6[1] (each)	mg/kg	0.01	0.1	0.003	0.003 or 30%
Lindane	mg/kg	0.01	0.1	0.003	0.003 or 30%
pp'DDT	mg/kg	0.01	0.1	0.003	0.003 or 30%
PCB – 7[2] (each)	mg/kg	0.01	0.1	0.003	0.003 or 30%

In harmonised monitoring programmes (national or international, e.g., for river basins), the use of agreed methods in all participating laboratories provides a common base for collecting comparable monitoring data.

Regardless of the analytical method used in the laboratory, the specific methodology should be carefully documented. In some water pollution reports it is customary to state that “Standard Methods” have been used throughout. Close examination may indicate, however, that this is not strictly true. In many laboratories, the “Standard Method” has been modified because of personal preferences of the laboratory staff, etc. In other cases the “Standard Method” has been replaced with a better one. Statements concerning the methods used in arriving at laboratory data should be clearly and honestly stated, if any deviation from the standard procedure occurs, proper validation of the analytical method is an absolute need. The methods used should be adequately referenced and the procedures applied exactly as directed. The recommended methods to be used in water laboratories are listed in Annex 1.

[1] fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene and benzo(1,2,3-cd)pyrene
[2] PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153 and PCB-180

Knowing the specific method, which has been used, the reviewer can apply the associated precision and accuracy of the method when interpreting the results. If the analytical methodology is in doubt, the data user may inquire the reliability of the result.

The advantages of strict adherence to accepted methods should not reduce efforts, investigations leading to improvements in analytical procedures. In spite of the value of accepted and documented methods, occasions do arise when a procedure must be modified to eliminate unusual interference, or to yield increased sensitivity. When modification is necessary, the revision should be carefully worked out and the revised method should be validated to accomplish the desired result. It is advisable to assemble data using both the regular and the modified procedure to show the superiority of the latter. Responsibility for the use of a non-standard procedure rests with the analyst and his supervisor, since such use represents a deviation from accepted practice.

In field surveys, the problem of transport of samples to the laboratory, or the need to analyse a large number of samples to arrive at gross values may require the use of rapid field (screening) methods. Such methods should be used with caution, and with a clear understanding that the results obtained do not compare in reliability with those obtained using standard laboratory methods. The fact that such screening methods have been used should be noted. The data user is entitled to know that approximate values have been obtained for screening purposes only, and that the results do not represent the precision and accuracy, which might be obtained in the laboratory.

1.3.2 Laboratory Facilities and Personnel

The quality of the laboratory work should be ensured by appropriate facilities including instrumentation, as well as by skilled personnel. Related issues will be discussed in more details in the following chapters of the guidance.

Depending on the size of the laboratory, e.g., more than 15-20 staff member, a quality manager should be appointed. The responsibility of this person includes: (a) supervision of the internal quality control measures in the laboratories, (b) ensure regular provision of spiked samples which are unknown for the analyst before the evaluation of the results, and (c) co-ordinate participation of the laboratories in performance testing programmes.

The appointment of quality manager is obligatory in laboratories having accreditation.

2 QUALITY REQUIREMENTS OF WATER QUALITY MONITORING

The background reports, particularly on the *Quality Assurance*, prepared by the UN/ECE Task Force on Monitoring and Assessment provide general guidance on the quality requirements and quality assurance needed for water quality monitoring. The present guidance gives more practical details on these subjects particularly to help laboratories in their ways for accreditation.

2.1 Quality Assurance, Quality Control in Water Laboratories

Because of the importance of monitoring data (analytical results) and the resulting actions, a programme to assure the reliability of the data is essential. It is recognised that most analysts practice analytical quality control to varying degrees, depending partly upon their training, professional ambitions, and partly upon the importance of the work they are doing. However, under the pressure of daily workload, analytical quality control may be easily neglected. Therefore, an established, routine internal quality control programme, applied to each analytical test, is important in assuring the reliability of the measurement results. When the implementation of the monitoring programme requires participation of several national, or international laboratories, there is a need for external quality control measures such as organisation and participation in performance testing schemes (intercalibration programmes) organised by dedicated institutions.

The quality control programme in the laboratory has two primary functions. First, the programme should monitor the reliability of the reported results. It should provide an answer to "How good (true) are the results submitted". This phase may be termed as "measurement of quality." The second function is the control of quality in order to meet the programme requirements. For example, the processing of spiked samples is the measurement of quality, while the use of analytical grade reagents is a control measure. As each analytical method has an analytical protocol (e.g., in international/national standards, or in Standard Operational Procedures compiled in the frame of most large international river basin management programme), so the quality control associated with that test must also involve definite steps to monitor and assure the correctness of the results. The steps in quality control vary with the type of analysis. For example, in the titrimetric measurements, standardisation of the titrant on a frequent basis is an element of qualify control. In an instrumental method, the check-out of instrument response and the calibration of the instrument in concentration units is also a quality control function. The variables, which can affect the final results should be considered and evaluated.

The guidance considers and provides recommendations for the control of the factors, which go into generating an analytical result, in order to ensure that the best possible result is obtained. A programme based upon these recommendations will give the analyst and the laboratory confidence in the reliability of the measurement results characterising the collected sample.

2.2 Requirements for Accreditation

Preparedness of water laboratories should be achieved before applying for accreditation. Part II. of the present guidance will help the laboratories with highlighting practical approaches (mainly technical requirements), however, it is strongly recommended to the candidate laboratories to follow the guidance in the ISO/IEC Guide 17025.

The present chapter focuses on some management requirements of ISO/IEC 17025.

The laboratory – which intends to be accredited – shall

- have managerial and technical personnel with the authority and resources needed to carry out their duties and to identify the occurrence of departures from the quality system or from the procedures for performing tests and/or calibrations, and to initiate actions to prevent or minimize such departures;
- have arrangements to ensure that its management and personnel are free from any undue internal and external commercial, financial and other pressures and influences that may adversely affect the quality of their work;
- have policies and procedures to ensure the protection of its clients' confidential information and proprietary rights, including procedures for protecting the electronic storage and transmission of results;
- have policies and procedures to avoid involvement in any activities that would diminish confidence in its competence, impartiality, judgment or operational integrity;
- define the organization and management structure of the laboratory, its place in any parent organization, and the relationships between quality management, technical operations and support services;
- specify the responsibility, authority and interrelationships of all personnel who manage, perform or verify work affecting the quality of the tests and/or calibrations;
- provide adequate supervision of testing and calibration staff, including trainees, by persons familiar with methods and procedures, purpose of each test and/or calibration, and with the assessment of the test or calibration results;
- have technical management which has overall responsibility for the technical operations and the provision of the resources needed to ensure the required quality of laboratory operations;
- appoint a member of staff as quality manager who, irrespective of other duties and responsibilities, shall have defined responsibility and authority for ensuring that the quality system is implemented and followed at all times, the quality manager shall have direct access to the highest level of management at which decisions are made on laboratory policy or resources;
- appoint deputies for key managerial personnel

The laboratory shall establish, implement and maintain a quality system appropriate to the scope of its activities. The laboratory shall document its policies, systems, programmes, procedures and instructions to the extent necessary to assure the quality of the test and/or calibration results. The system's documentation shall be

communicated to, understood by, available to, and implemented by the appropriate personnel.

The laboratory's quality system policies and objectives shall be defined in a quality manual. The overall objectives shall be documented in a quality policy statement. The quality policy statement shall be issued under the authority of the chief executive. It shall include at least the following:

- the laboratory management's commitment to good professional practice and to the quality of its testing and calibration in servicing its clients;
- the management's statement of the laboratory's standard of service;
- the objectives of the quality system,
- a requirement that all personnel concerned with testing and calibration activities within the laboratory familiarize themselves with the quality documentation and implement the policies and procedures in their work;
- the laboratory management's commitment to compliance with ISO/IEC 17025 Standard.

The quality manual shall include or make reference to the supporting procedures including technical procedures. It shall outline the structure of the documentation used in the quality system. The quality manual should include:

- documents of the critical procedures within the laboratory;
- Standard Operating Procedures for the analytical methods;
- Standard Operating Procedures for the use of instruments;
- Performance characteristics of each method/matrix combination.

The roles and responsibilities of technical management and the quality manager, including their responsibility for ensuring compliance with this International Standard, shall be defined in the quality manual.

The laboratory shall established and maintain procedures to control all documents that form part of its quality system (internally generated or from external sources), such as regulations, standards, other normative documents, test and/or calibration methods, as well as drawings, software, specifications, instructions and manuals.

The laboratory shall establish and maintain procedures for the review of requests, tenders and contracts. The policies and procedures fro these reviews leading to a contract for testing and/or calibration shall ensure that:

- the requirements, including the methods to be used, are adequately defined, documented and understood;
- the laboratory has the capability and resources to meet the requirements;
- the appropriate test and/or calibration method is selected and capable of meeting the clients' requirements.

The laboratory shall afford clients or their representatives cooperation to clarify the client's request and to monitor the laboratory's performance in relation to the work performed, provided that the laboratory ensures confidentiality to other clients.

The laboratory shall periodically, and in accordance with a predetermined schedule and procedure, conduct internal audits of its activities to verify that its operations continue to comply with the requirements of the quality system. The internal audit programme shall address all elements of the quality system, including the testing and/or calibration activities. It is the responsibility of the quality manager to plan and organize audits as required by the schedule and requested by management. Such audits shall be carried out by trained and qualified personnel who are, wherever resources permit, independent of the activity to be audited.

In accordance with a predetermined schedule and procedure, the laboratory's executive management shall periodically conduct a review of the laboratory's quality system and testing and/or calibration activities to ensure their continuing suitability and effectiveness, and to introduce necessary changes or improvements. The review shall take account of:

- the suitability of policies and procedures;
- reports from managerial and supervisory personnel;
- the outcome of recent internal audits;
- corrective and preventive actions;
- assessments by external bodies;
- the results of interlaboratory comparisons or proficiency tests;
- changes in the volume and type of the work;
- client feedback;
- complaints;
- other relevant factors, such as quality control activities, resources and staff training.

PART II.

3 COLLECTION OF SAMPLES FROM THE AQUATIC ENVIRONMENT

The design of the sampling plan is part of the monitoring cycle, whereas the implementation of the sampling belongs to the measurement cycle. Collection of the representative samples should be the responsibility of the laboratory staff. Because collection of samples from different environmental matrices can be considered as the first step in the measurement cycle and very much dependent on the analytical work it is desirable to collect the samples by laboratory personnel.

Objective of the sampling activities in analytical procedures is to obtain a representative quantity of material small enough to be handled and transported to a laboratory. Sampling and sample pretreatment often seem to be a quite easy thing to do and thus in many cases young and less experienced personnel is in charge of the sampling procedure. Considering that the sampling procedure is the first step of the analysis it should be pointed out that any mistakes which were made in taking the sample will cause an error in the final data regardless of the qualification of the analyst in the laboratory and the superior quality of instruments used. Thus it is necessary to consider the sampling step as one of the most important steps in the whole measurement cycle and the sampling staff should be conscious of this.

There are standard sampling procedures described in different international and national standards, included in operational protocols. ISO 5667-1-17 series deals with the design of sampling programmes; sampling techniques; preservation and handling of samples; sampling from lakes, rivers and streams; sampling of waste waters, bottom sediments, sludges; quality assurance of environmental water sampling and handling; preservation and handling of sludge and sediment samples; biotesting of samples; sampling of suspended sediments. Therefore, in this guidance some general sampling considerations are reviewed and a separate chapter (3.1.) is dedicated to sample collection from sediments because of the special requirements.

The objective of sampling is to collect a portion of material small enough in volume to be transported conveniently and yet large enough for analytical purposes while still accurately representing the material being sampled. This objective implies that the relative proportions or concentrations of all pertinent components will be the same in the samples as in the material being sampled, and that the sample will be handled in such a way that no significant changes in composition occur before the tests are made (APHA, AWWA, WEF 1998).

Grab samples are single samples collected at a specific spot at a site over a short period of time (typically seconds or minutes). Thus, they represent a "snapshot" in both space and time of a sampling area. Discrete grab samples are taken at a selected location, depth, and time. Depth-integrated grab samples are collected over a predetermined part or the entire depth of a water column, at a selected location and time in a given body of water.

Composite samples should provide a more representative sampling of heterogeneous matrices in which the concentration of the analytes of interest may vary over short periods of time and/or space. Composite samples can be obtained by combining portions of multiple grab samples or by using specially designed automatic sampling devices. Sequential (time) composite samples are collected by using continuous, constant sample pumping or by mixing equal water volumes collected at regular time intervals. Flow-proportional composites are collected by continuous pumping at a rate proportional to the flow, by mixing equal volumes of water collected at time intervals that are inversely proportional to the volume of flow, or by mixing volumes of water proportional to the flow collected during or at regular time intervals.

Because of the inherent instability of certain properties and compounds, composite sampling for some analytes is not recommended where quantitative values are desired.

When samples are collected from a river or stream, observed results may vary with depth, stream flow, and distance from each shore. Selection of the number and distribution of sites at which samples should be collected depends on study objectives, stream characteristics, available equipment, and other factors. If equipment is available, take an integrated sample from top to bottom in the middle of the main channel of the stream or from side to side at mid-depth. If only grab or catch samples can be collected, preferably take them at various points of equal distance across the stream; if only one sample can be collected, take it in the middle of the main channel of the stream and at mid-depth.

Rivers, streams, lakes, and reservoirs are subject to considerable variations from normal causes such as seasonal stratification, diurnal variations, rainfall, runoff, and wind. Choose location, depth, and frequency of sampling depending on local conditions and the purpose of the investigation.

Although well pumping protocols depend on the objectives of an investigation and other factors such as well characteristics and available equipment, a general rule is to collect samples from wells only after the well has been purged sufficiently to ensure that the sample represents the groundwater. It will be necessary to pump at a specified rate to achieve a characteristic drawdown, if this determines the zones from which the well is supplied; record purging rate and drawdown, if necessary. By using methods with minimal drawdown, purging volumes can be reduced significantly.

Sample carefully to ensure that analytical results represent the actual sample composition. Important factors affecting results are the presence of suspended matter or turbidity, the method chosen for removing a sample from its container, and the physical and chemical changes brought about by storage or aeration. Detailed procedures are essential when processing (blending, sieving, filtering) samples to be analyzed for trace constituents, especially metals and organic compounds. Carefully consider the technique for collecting a representative sample and define it in the sampling plan.

The type of sample container used is of utmost importance. Test sample containers and document that they are free of analytes of interest, especially when sampling and analyzing for very low analyte levels. Containers typically are made of plastic or glass, but one material may be preferred over the other. For example, silica, sodium, and

boron may be leached from soft glass but not plastic, and trace levels of some pesticides and metals may sorb onto the walls of glass containers. Thus, hard glass containers are preferred. For samples containing organic compounds, do not use plastic containers except those made of fluorinated polymers such as polytetrafluoroethylene (PTFE).

Some sample analytes may dissolve (be absorbed) into the walls of plastic containers; similarly, contaminants from plastic containers may leach into samples. Avoid plastics wherever possible because of potential contamination from phthalate esters. Container failure due to breakdown of the plastic is possible. Therefore, use glass containers for all organics analyses such as volatile organics, semivolatile organics, pesticides, PCBs, and oil and grease. Some analytes (e.g., bromine-containing compounds and some pesticides, polynuclear aromatic compounds, etc.) are light-sensitive; collect them in amber-colored glass containers to minimize photodegradation.

Because of variability from analytical and sampling procedures (i.e., population variability), a single sample is insufficient to reach any reasonable desired level of confidence. If an overall standard deviation (i.e., the standard deviation of combined sampling and analysis) is known, the required number of samples for a mobile matrix such as water may be estimated as follows:

$$N \geq \frac{(ts)^2}{U}$$

where:

N = number of samples,
t = Student-t statistic for a given confidence level,
s = overall standard deviation, and
U = acceptable level of uncertainty.

Complete and unequivocal preservation of samples, is a practical impossibility because complete stability for every constituent never can be achieved. At best, preservation techniques only retard chemical and biological changes that inevitably continue after sample collection.

To minimize the potential for volatilization or biodegradation between sampling and analysis, keep samples as cool as possible without freezing. No single method of preservation is entirely satisfactory; choose the preservative with due regard to the determinations to be made. Use chemical preservatives only when they do not interfere with the analysis being made.

Methods of preservation are relatively limited and are intended generally to retard biological action, retard hydrolysis of chemical compounds and complexes, and reduce volatility of constituents. Preservation methods are limited to pH control, chemical addition, the use of amber and opaque bottles, refrigeration, filtration, and freezing.

3.1 Sample Collection from Sediments

Three major types of solid particles (particulate matter) can be distinguished in rivers and lakes, even though this classification is not absolute. One type can be converted into another by the changes in water velocity. Those types are:

Suspended matter - particles maintained by water turbulence in suspension above the river bed or lake bottom. In rivers the total amount and particle size vary greatly with stream flow. In lakes the amount is usually small, less than 10mg/l, and consists mostly of organic lacustrine detritus and very fine soil material;

Bedload - that part of the particulate matter which remains in almost constant contact with the river bed and is moved by rolling, sliding or hopping much more slowly than the water velocity;

Deposited matter - results from a decrease in water energy. This leads to settling, the rate of which depends on the particle size.

Guidance for sediment sampling can be obtained from the ISO Guide 5667-12: Guidance on sampling bottom sediment and ISO Guide 5667-17: Guidance on sampling of suspended sediments.

3.1.1 Sampling Equipment

The procedures and apparatus applied for sediment sampling depend on the type of sediment required for analysis. The procedures and the equipment used for sampling suspended sediments are different from those required for bottom sediment. In general, care must be taken not to lose fine fractions since the association (adsorption) of analytes is largest on small particles. During bottom sediment sampling the sampler must be usually able to maintain the integrity of the layers, but it is very difficult particularly in the case of sampling fast-flowing river bottom sediment.

3.1.1.1 Suspended sediment samplers

Samplers used for suspended sediments must allow the collection of a sample representative of the water-sediment mixture at the sampling point or sampling zone at the time of sampling and in amount enough to carry out all of the required analysis. Samplers are of four general types:

* Integrating samplers
* Grab samplers
* Pumping (centrifuging) samplers
* Sedimentation traps

The integrating samplers are designed in a way that the intake nozzle is oriented into, and parallel to the flow. As a result, the water-sediment mixture moves from the stream into the intake with minimum acceleration, thus providing the most accurately the representative sample.

In smaller rivers, direct hand sampling can be performed by wading, using a simple grab sampler, such as a bucket if that is all that is available. If the suspended sediment load is sufficiently high, grab or depth-integrating samplers may be used followed by pressure, or vacuum filtration through a 0.45 μm filtration system.

Pumped centrifugation can provide relatively large amount of sediment sample, which might be required for trace organic analysis, but it needs a special portable centrifuge designed for such type of sample collection.

In lakes, the first two types are unlikely to provide enough material after filtration for even the most basic analyses. Most of the published work on the suspended matter in lakes has used sedimentation traps, although microbial processes continuing within them during the lengthy residence times required to obtain even small samples, and the complex physics of trap entry raise doubts about how representative the analyses may be. Sedimentation traps for use in lakes and reservoirs are cylinders of plastic for metallic determinands, and glass or metal for organic compounds. The cylinder should have a height-to-width ratio larger than five, with nothing above the opening such as lattices, lids or collars. It is necessary to prevent the mooring system from moving by using an appropriate sub-surface float. Traps should be retrieved after no more than one month to reduce mineralization and microbial degradation of suspended organic matter.

3.1.1.2 Bottom sediment samplers

Because the topmost layer of the sediment is the most recent and is the site of the most intensive microbiological activity, it is usually important that the sampler does not stir the sediment surface and/or cause change in the sediment layers. Thus, the sampler must be lowered so as not to create a pressure wave that might displace the softest surface sediments. The sampler must penetrate far enough into the sediments to include the desired layers, but not so far that the sediment spills over the top.

For different sediment types the recommended samplers are summarized in Table 2.

Grab samplers

Grab samplers are more commonly used than core samplers for collecting deposited sediments as they are often much lighter and in some circumstances much easier to use. There is a large number of variations of bed grabbers. They consist of one or more hinged buckets which close whilst being raised. During scissors-like closing of the buckets, sediment is enclosed by them, providing disturbed samples. Probe depths vary from 5 cm to 50 cm, depending upon the size and mass of the sampler and the structure of the bed material. Due to the grab construction, there is a large chance of losing part of the finer fraction and/or the top layer. Grabs are available in a variety of designs.

In general the scissor grab is most suited for sampling sediment beds consisting of silt and/or sand. It is not suitable for sampling peat or clays. A sample taken with a scissor grab will always be disturbed. Inaccuracies arise because of washing away of the fine fractions. Depth of the penetration is unknown and dependent on the nature of the bed for any particular instrument.

Table 2. Sediment types and recommended samplers.

Type of sediment	Sampler
Gravel	Grab systems
Sand	Both grab and corer systems can be used. A sand bed can be very hard and thus prove difficult for light weight grabs and manually operated corer systems
Clay	It may be necessary to use a corer because grab systems often can not penetrate easily into the clay
Peat	A difficult medium to sample but it is sometimes possible to use a corer system or a special peat borer
Consolidated silt	Both grab and corer can be used. If a grab is used, it is not possible to determine the sample penetration depth
Unconsolidated silt	Grab systems are not suitable as they are prone to sinking through the soft layer. Corer systems are better but when a frame is used at great depth care is essential to prevent the frame from sinking through the soft layer. More support can usually be given to prevent this by adding large plates to the feet of the frame.

Core samplers

Sampling using a core sampler is based on a principle of driving a hollow tube into the bed so that the sediment is pushed into it. A sample is obtained by pulling the tube out of the bed. The tube can be inserted into a bed by means of its weight, vibration device or manually.

In manually operated corers (e.g., piston drill, Beeker sampler, sealed core sampler, Vrijwit drill, etc.) the tube is pushed into the bed by means of rods. Penetration is generally up to maximum 2 meters, depending on the nature of bed materials. Gravels are unlikely to be suited to this sampling method. Because extension rods are used, there can be problems in obtaining samples when working from the bank where a distance of more than 4 m must be bridged by rods. Due to the movement of the vessel, it is often difficult to obtain good samples from a boat. However, it is possible to obtain reliable samples in a river depth of approximately 2 m; beyond this, a diver may need to be employed.
Mechanically operated sampling devices employ usually their weight for penetrating into the bed. In the gravity corer ("Falling bomb" sampler) the core tube is mounted in a weighted holder, which is dropped freely from a vessel and penetrates the sediment. The method is fast and efficient because it is not necessary for the vessel to be anchored. This sampler is not suitable for use in unconsolidated sediments.

In the "Jenkins mud sampler", the corer is mounted in a frame and due to its large mass sinks into bed. Once the suspension cable is slackened sufficiently, a closing mechanism is activated which shuts off the sample tube by the means of hinged arms. This sampler is suitable for investigation of very soft beds, it is not suitable for hard sediment beds.

The Craib corer consists of a core tube mounted in a frame. When it is lifted out of the sediment layer, the core tube is first closed off at the top by a valve. As soon as the bottom is free of the bed, it is closed off by a ball.

The Easy All corer's mass can be increased to approx. 110kg. After the sample has been taken, the core tube is shut off at the top and the bottom by means of valves. The filled core tube can be removed from the holder completely once it is aboard.

3.1.2 Storage, Transport and Preservation of Sediment Samples

3.1.2.1 Sample Containers

Polyethylene, polypropylene, polycarbonate and glass containers are recommended for most sampling situations, although glass jars have the advantage that the condition of their internal surface is more readily apparent, and they can be sterilised more easily than most plastic materials prior to use in microbiological sampling situations.

Glass containers should also be used when organic constituents are to be determined, whereas polyethylene containers are preferable for sampling those determinands that are major constituents of glass (e.g., sodium, potassium, boron and silicon) and for sampling of trace metallic moieties (e.g., mercury). These containers should only be used if preliminary tests indicate acceptable levels of contamination. If glass containers are used for storing sediments with pore waters, which are weakly buffered, then borosilicate rather than soda glass containers should be chosen.

3.1.2.2 Handling of Sediment Samples

Suspended sediment

As soon as possible after collection, the sample should be filtered. The filtrate can then be used for measuring the dissolved constituents. The following sample containers and preservation procedures are recommended:

- Samples for analysis of carbon, heavy metals, nitrogen and phosphorus can be stored in polyethylene or polypropylene bag or jar frozen to -20°C for the period of max. 6 months.
- Samples for analysis of chlorinated hydrocarbons, pesticides and oil pollution can be stored in glass jar or aluminum canister extracted immediately, or frozen to -20°C and extracted as soon as possible.

The analysis of a suspended sediment sample is often limited on account of the difficulty in obtaining sufficient material for the several sub-samples required for the different analyses. A composite of a large number of representative samples may be necessary.

Bottom sediment

In practice it has become apparent that every project or investigation sets its own particular demands in the field of sample treatment. The investigation plan prepared for the field sampling should include a section on the treatment of the samples. This plan should take into account the particular aim of the project and the requirements for the sample treatment given by the receiving analyst.

When transferring samples from the collection equipment to the storage container, care should be taken to ensure the continuance of anaerobic conditions if appropriate to the planned analysis. The maintenance of anaerobic conditions will to a large extent depend on the equipment being used. A practice run may be found useful to refine any techniques developed. In addition, if trace organics are to be studied, use of some plastic implements during sub-sampling may contribute to interference. Similarly, the use of a metal spatular should be avoided if trace metals are of interest. The type and composition of sample transfer tools should be noted in the field report.

Sediment samples should generally be kept in glass containers and stored and transported cool. If it is necessary to keep them longer than one month, then this should be done in a deep freezer, giving due regard to the physicochemical changes that can occur to colloids on freezing. For example, changes in de-watering characteristics may be observed when specific laboratory sample preparations are used. In all cases sample containers should be delivered to the laboratory tightly sealed and protected from light and excessive heat, because the sample may change rapidly due to gas exchange, chemical reactions and the metabolism of organisms. The build up of gas pressures in the sample container, due to anaerobic digestion, should not be overlooked, and it may therefore be necessary periodically to release pressure from the container. This may become necessary if temperature regulation cannot be provided in warm climates.

If freezing the sample is chosen as the preferred method of preservation as defined by the sampling programme and specified analytical method, the notice should be taken of following:

- It is essential for the sample to be completely thawed before use, as the freezing process may have the effect of concentrating some components in the pore water of the inner part of the sample, which substantially freezes last. The freezing of samples can lead to a loss of analytes from pore-water solution by absorption/adsorption on the precipitating compounds. When the sample thaws, dissolution may be incomplete, and thus erroneous results for pore water parameters may be produced.
- Chemical preservation techniques should only be used after careful assessment of the project needs, the requirements of the analytical method and with the specific guidance of the receiving laboratory about the techniques required for homogenisation of the sample with the preservative. For example, mineral acid may be added in an attempt to arrest or inhibit anaerobic digestion of organic matter if a study of organic acids is being made. Separate sub-samples, therefore, may be required prior to freezing.

All preservation steps should be recorded in a site report and the temperature measured and recorded on site. If appropriate, other physical and chemical parameters should be determined on site or as soon as possible after sample collection.

3.1.3 Selection of Particle Size

In the literature are still very differing proposals for the choice of the grain size fraction for analyses. It is a fact that the organic micropollutants are mainly adsorbed on the organic part of the sediment, which can be found with increasing amount in the small grain-size fractions but it is also valid for the inorganic micropollutants. The larger particles, mainly quartz (sand), are considered as diluting material.

The sediment sample has to be fractionated prior to sample processing and analysis. Selection of the fraction for the analysis depends, similarly to the sampling type, on the general aim of the sediment analysis, and it should reflect the distribution of the particular analyte as a function of the sediment particle size. Thus, any sediment analysis program should be preceded by an agreement on the fraction to be analyzed (e.g., 4 - 200 µm or < 63 µm). Because of the tedious sieving process for grain-size smaller than about 50 µm, grain- size fractions around this value are chosen in many cases for practical reasons. The clay-silt fraction, smaller than 63 µm, is widespread in different monitoring programmes. Sieving of the sediment should be done in the wet state at the sampling site through appropriate sieves. Sieves used for fractionation have to be made from material that will not interfere with the analytes.

3.1.4 Drying of Sediment

Drying is performed mainly with four methods

- air drying at room temperature or slightly elevated temperatures (50 °C). This drying procedure takes up to several days and a relative high amount of water remains in the sample depending on its nature
- drying in air at 105 °C in drying oven and cooling in a desiccator. This procedure is only recommend for determination of non-volatile organic compounds and used for determination of the dry residue (moisture content) of the air-dried sample.
- freeze-drying, which seems to be a very gentle drying method, but loss of organic material cannot be excluded.
- grinding of sediment with anhydrous sodium sulphate in the case of trace organic analysis seems to be a fast and gentle method, but the high water content sometimes makes troubles during the extraction procedure.

In any cases the dry weight of the sediment has to be determined with a part of the sample because the concentration of analytes should be related to dry sediment mass, expressed as mg/kg of dry sediment.

4 PREREQUISITES OF QUALITY WORK IN LABORATORIES

Architectural design of environmental (water) laboratories not subject of this guideline, however, it is important to note that good, high quality laboratory work requires appropriate planning, design and construction of the laboratory complex. Depending on the planned use of the laboratory, i.e., for research and/or monitoring; chemical, radiochemical, biological or microbiological analyses, etc., appropriate space and basic laboratory facilities should be available.

This chapter provides guidance for laboratory managers and staff concerning the laboratory services, instrumentation, etc., needed to support and ensure the quality of the work in the laboratory.

4.1 Laboratory Services

The quality of the work laboratory analyses involves consideration and control of several factors, which affect the production of reliable data. The quality of the laboratory services available to the analyst must be included among these variables. An abundant supply of distilled water, free from interferences and other undesirable contaminants, is an absolute necessity. An adequate source of clean, dry, compressed air is needed. Electrical power for routine laboratory use and voltage-regulated sources for delicate electronic instrumentation must be provided.

The ways of maintaining the quality of these services in the laboratory are provided in the following.

4.1.1 Distilled-Deionised Water

Distilled or deionised (demineralised) water is used in the laboratory for dilution, preparation of reagent solutions, and final rinsing of glassware. Ordinary distilled water is usually not pure. It may be contaminated by dissolved gases and by materials leached from the container in which it has been stored. Volatile organics distilled over from the feed water may be present, and non-volatile impurities may occasionally be carried over by the steam, in the form of a spray. The concentration of these contaminants is usually quite small and distilled water can be used for many analyses without further purification. However, it is highly important that the still, storage tank, and any associated piping be carefully selected, installed, and maintained in such a way as to assure minimum contamination.

Water purity has been defined in different ways, but one generally accepted definition states that high purity water is water that has been distilled and/or deionised so that it will have a conductivity of 2 µS/cm, or smaller. This definition is satisfactory as a base to work from, but for more critical requirements, Table 3 shows the degrees of purity.

Table 3. Water purity on the basis of dissolved salts.

Degree of Purity	Maximum Conductivity (µS/cm)	Approximate Concentration of Dissolved Salts (mg/l)
Pure	10	2-5
Very Pure	1	0.2-0.5
Ultrapure	0.1	0.01-0.02

For special purposes, all-glass distillation unit may be preferable to the metal still. The all-glass distillation units are usually smaller, and of more limited capacity than the metal stills. The all-glass still produced a product, which had substantially lower contamination from zinc, copper, and lead. Other analyses have indicated the same general relationship, except that a boron concentration of 100 µg/litre was found in water from the all-glass still on one occasion. This was probably related to the length of time the distillate had remained in the glass storage reservoir.

All distillation units require periodic cleaning to remove solids, which have been deposited from the feed water. Hard water and high dissolved solids content promote scale formation in the evaporator, and cleaning frequency will thus depend on the quality of the feed water. The boiler of an all-glass unit should be drained daily and refilled with clean water. Build-up of scale is easily detected, and the boiler and condenser coils should be cleaned at frequent intervals. Metal stills should be dismantled and cleaned at regular intervals. Cleaning should always be in accordance with the manufacturer's instructions.

Pre-treatment of the incoming feed water will often improve distillation performance and raise the quality of the distillate. For example, preliminary softening of hard water removes calcium and magnesium prior to distillation. This reduces scale formation in the boiler and condenser, thereby reducing maintenance service. These softeners employ the ion exchange principle using a sodium chloride cycle, and are relatively inexpensive to operate. A carbon filtration system, installed at the feed water intake, will remove organic materials, which might subsequently be carried over in the distillate. If trace concentrations of ions, organic substances are of major concern, the distillate may be further treated as described later.

A piping system for delivering distilled/deionized water to the area of use within the laboratory is a convenient feature. In this case, special care should be taken that the quality of the water is not degraded between the still/deionizer and the point of use. Piping may be of tin, tin-lined brass, stainless steel, plastic, or chemically resistant glass, depending on the quality of the water desired and on available funds. Tin is best, but is also very expensive. As a compromise, plastic pipe, or (Teflon) glass pipe with Teflon O-rings at all connecting joints is satisfactory for most purposes. The glass pipe has an obvious advantage when freedom from trace amounts of organic materials is important.

When there is no piped-in supply, distilled water will be transported to the laboratory and stored in polyethylene or glass bottles. If stored in glass containers, distilled water will gradually leach the more soluble materials from the glass and cause an increase in dissolved solids. Therefore, only borosilicate-free glass containers should be used. Polyethylene bottles contain organic plasticizers, and traces of these materials may be leached from the container walls. These are of little consequence, except in some organic analyses. Rubber stoppers often used in storage containers contain leachable materials, including significant quantities of zinc. This is usually no problem, since the water is not in direct contact with the stopper. However, the analyst should be aware of the potential for contamination, especially when the supply is not replenished by frequent use.

The delivery tube may consist of a piece of glass tubing, which extends almost to the bottom of the bottle, and which is bent downward above the bottle neck, with flexible tubing attached for mobility. Vinyl tubing is preferable to rubber, because it is less leachable. The vent tube in the stopper should be protected against the entrance of dust.

Ordinary distilled water is quite adequate for many analyses, including the determination of major cations and anions. Certain needs may require the use of double- or even triple-distilled water. Re-distillation from an alkaline permanganate solution can be used to obtain a water with low organic background. Certain analyses require special treatment or conditioning of the distilled water.

The quality of the distilled water should be checked according to the given determinands, however, it is always include in the method blank determinations when it is part of the analytical procedures (e.g., trace organic analysis).

4.1.1.1 Ammonia-Free Water

Removal of ammonia can be accomplished by shaking ordinary distilled water with a strong cation exchanger, or by passing distilled water through a column of such material. The ion-free water described below is also suitable for use in the determination of ammonia.

The ammonia content of this water should be below the detection limit, as measured in the blank solution.

4.1.1.2 Carbon-Dioxide-Free Water

Carbon-dioxide-free water may be prepared by boiling distilled water for 15 minutes and cooling to room temperature. As an alternative, distilled water may be vigorously aerated with a stream of inert gas for a period sufficient to achieve saturation and CO_2 removal. Nitrogen is most frequently used. The final pH of the water should lie between 6.2 and 7.2. It is not advisable to store CO_2-free water for extended periods.

4.1.1.3 Ion-Free Water

A multi-purpose high purity water, free from trace amounts of the common ions, may be conveniently prepared by slowly passing distilled water through an ion-exchange column containing strongly acidic cation-exchange resin in the hydroxyl form. Resins of a quality suitable for analytical work must be used. By using a fresh column and high quality distilled water, the water corresponding to designation for referee reagent water (maximum 0.1 mg/l total matter and maximum conductivity of 0.1 μS/cm) can be obtained. This water is suitable for use in the determination of ammonia, trace metals, and low concentrations of most cations and anions. It is not suited to some organic analyses, however, because this treatment may add organic contaminants to the water by contact with the ion-exchange materials.

4.1.1.4 Organic-Free Water

When determining trace organics by solvent extraction and gas chromatography, distilled water with sufficiently low background may be extremely difficult to obtain. In this case, pre-extraction of the water with the solvent used in the respective analysis may be helpful in eliminating undesirable peaks in the blank, or use the more expensive water purification units manufactured by several companies and available on the market.

4.1.2 Compressed Air

The quality of compressed air required in the laboratory is usually very high, and special attention should be given to producing and maintaining clean air until it reaches the outlet. Oil, water, and dirt are undesirable contaminants in compressed air, and it is important to install equipment, which generates dry, oil-free air. When pressures of less than 50 psi are required, a rotary-type compressor, using a water seal and no oil, eliminates any addition of oil, which would subsequently have to be removed from the system. Large, horizontal, water-cooled compressors will usually be used when higher pressures are required.

When the compressed air entering the laboratory is of low quality, an efficient filter should be installed between the outlet and the point of use to trap oil, moisture, and other contaminants. As an alternative, high quality compressed air of the dry grade is commercially available in cylinders when no other source exists.

4.1.3 Electrical Supplies

An adequate electrical system is indispensable to the modern laboratory. This involves having appropriate voltage (110-220-240-380 V) sources in sufficient capacity for the type of work that must be done. Requirements for satisfactory lighting, proper functioning of sensitive instruments, and operation of high current devices must be considered. Any specialized equipment may present unusual demands on the electrical supply.

Due to the special type of work, requirements for a laboratory lighting system are quite different from those in other areas. Accurate readings of glassware graduations and other measuring lines must be made. Titration endpoints, sometimes involving subtle changes in colour or shading, must be observed. Levels of illumination, brightness, and

location of light sources should be controlled to facilitate ease in making these measurements and to provide maximum comfort for the employees.

Spectrophotometers, flame photometers, atomic absorption equipment, gas chromatographs, etc. have complicated electronic circuits, which require relatively constant voltage to maintain stable, drift-free instrument operation. If the voltage to these circuits varies, there is a resulting change in resistance, temperature, current, efficiency, light output, and component life. These characteristics are interrelated, and one can not be changed without affecting the others. Voltage regulation is therefore necessary to eliminate these conditions. Many instruments have built-in voltage stabilizers, which perform this function satisfactorily. In the absence of these, a small, portable, constant-voltage transformer should be placed in the circuit between the electrical outlet and the instrument. When requirements are more stringent, special transformer-regulated circuits can be used to supply constant voltage.

Electrical heating devices (hot plates, muffle furnaces, water baths and laboratory ovens) provide desirable heat sources. Care must be taken to ground all equipment, which could constitute a shock hazard.

Special attention should be paid in laboratories where electric supply shuts down temporarily time-to-time, for different time periods. Several instruments can be damaged, or data lost from sudden stop of electricity. Therefore, it is important to establish power cut-off free units, which provide electricity continuously when central electric power-supply stops.

4.2 Instrumentation

The modem analytical laboratory depends very heavily upon instrumentation. Analytical instrumentation, to a certain extent, is always in the development stage, with manufacturers continually redesigning and upgrading their products, striving for better durability and sensitivity, and improved automation, particularly due to computerization. The laboratory supervisors and stuff members should consider the competing markets, a stream of advertising brochures, announcements, and catalogues of newly available equipment. Consequently, the selection and purchase of analytical equipment is should be based on careful considerations. Table 4. lists the instruments most commonly used in aquatic environmental analysis.

Table 4. List of instruments used in aquatic environmental analysis

Balances with different sensitivity: analytical, etc.,
pH meter, ion-selective electrodes, conductivity meter
Spectrophotometers
- a. Visual and Ultraviolet
- b. Infrared
- c. Fluorescence
- d. Atomic absorption (AAS) with flame atomization or electrothermic atomization

Inductively Coupled Plasma (ICP) with
- a. Atomic Emission Spectrophotometer
- b. Mass Spectrometer

Polarograph
Total and Dissolved Organic Carbon Analyzer (TOC/DOC)
Adsorbable/Extractable Organic Halogen Analyzer (AOX/EOX)
Gas Chromatographs (GC) with different detectors:
- a. FID
- b. ECD
- c. N & PD
- d. PID
- e. FTIR
- f. MS (MS-MS)

Ion-chromatograph (for anions and/or cations)
High Pressure Liquid Chromatograph (HPLC) with:
- a. DAD
- b. Fluorescence Detector
- c. MS (MS-MS)

These represent basic equipment used in routine work and more sophisticated instruments for special research and monitoring purposes. Further, operation and maintenance of these instruments ought to be a primary consideration in production of satisfactory data. Obviously, a fundamental understanding of instrument design will assist the analyst in the correct use of the instrument and in some cases aid in detecting instrumental failures.

More details on the different instruments are given in Annex 3.

4.3 Laboratory Glassware

The measurement of trace constituents in water demands methods capable of maximum sensitivity. This is especially true for metals and trace organics such as pesticides, as well as for the determination of ammonia and phosphorus. Depending on the parameter specific glassware is needed. In addition to sensitive methods, however, there are other areas that require special consideration. One such area is that of the cleanliness of laboratory glassware. Obviously, the very sensitive analytical systems are more sensitive to errors resulting from the improper use or choice of apparatus, as well as to contamination effects due to an improper method of cleaning the apparatus. The purpose of this chapter is to discuss the kinds of glassware available, the use of volumetric ware, and various cleaning requirements.

4.3.1 Types of Glassware

Laboratory vessels serve three functions: storage of reagents, measurement of solution volumes and confinement of reactions. For special purposes, vessels made from materials such as porcelain, nickel, iron, aluminum, platinum, stainless steel, and plastic may be employed to advantage. Glass, however, is the most widely used material of construction. There are many grades and types of glassware from which to choose, ranging from normal glass to others possessing specific properties such as resistance to thermal shock, alkali, low boron content, and super strength. Soft-glass containers are usually relatively soluble, and therefore are not recommended for general use, especially for storage of reagents. The best glassware of the modern analytical laboratory is made of highly resistant borosilicate glass, such as that manufactured under the name "Pyrex" or others. This glassware is satisfactory for all basic analytical work in the laboratory.

Depending on the particular manufacturer, various trade names are used for specific brands possessing special properties such as resistance to heat, shock, alkalies, etc. Examples of some of these follow:

a. Kimax- or Pyrex-brand glass is a relatively inert all-purpose borosilicate glass.

b. Vycor-brand glass is a silica glass (96%) made to withstand continuous temperatures up to 900°C and can be down-shocked in ice water without breakage.

c. Corning brand glass is claimed to be 50 times more resistant to alkalies than conventional ware and practically boron free (max. 0.2%).

d. Ray~Sorb- or Low-Actinic-brand glass is for use with light-sensitive material.

e. Corex-brand labware is harder than conventional borosilicates, better able to resist clouding and scratching.

The use of plastic vessels, containers and other apparatus made of Teflon, polyethylene, polystyrene and polypropylene has increased markedly over recent years. Some of these materials, such as Teflon, are quite expensive; however, Teflon stopcock plugs have practically replaced glass plugs in burets, separatory funnels, etc. because lubrication to avoid sticking or "freezing" is not required. Polypropylene, a methylpentene polymer, is available as laboratory bottles, graduates, beakers and even volumetric flasks. It is crystal clear, shatter-proof, autoclavable and chemically resistant. Some points to consider in choosing glassware and/or plastic-ware are:

- Unless instructed otherwise, borosilicate or polyethylene bottles are to be used for the storage of reagents and standard solutions.
- Certain dilute metal solutions may absorb on glass container walls over long periods of storage. Thus, dilute metal standard solutions are prepared fresh at the time of analysis.
- For some operations, disposable glassware is used. One example is the use of disposable test tubes as sample containers.

- Plastic bottles of polyethylene and/or Teflon have been found satisfactory for the shipment of water samples. Strong mineral acids (such as sulphuric acid) and organic solvents will readily attack polyethylene and are to be avoided.
- Borosilicate glassware is not completely inert, particularly to alkalies, therefore, standard solutions of silica, boron and the alkali metals are usually stored in polyethylene bottles.

4.3.2 Glassware for Volumetric Analyses

By common usage, accurately calibrated glassware for precise measurements of volume has become known as volumetric glassware. This group includes volumetric flasks, volumetric pipets and accurately calibrated burets. Less accurate types of glassware including graduated cylinders, serological and measuring pipets also have specific uses in the analytical laboratory, when exact volumes are unnecessary.

The precision of volumetric work depends in part upon the accuracy with which volumes of solutions can be measured and there are certain sources of error, which must be carefully considered. The volumetric apparatus must be read correctly; that is, the bottom of the meniscus should be tangent to the calibration mark. There are other sources of error, however, such as changes in temperature, which result in changes in the actual capacity of glass apparatus and in the volume of the solutions. The capacity of an ordinary glass flask of 1000 ml volume increases 0.025 ml per 1°C rise in temperature, but if made of borosilicate glass the increase is much less. 1000 ml of water or of most 0.1 N solutions increases in volume by approximately 0.20 ml per 1°C increase at room temperature. Thus solutions must be measured at the temperature at which the apparatus was calibrated. This temperature (usually 20°C) will be indicated on all volumetric ware.

Volumetric apparatus is calibrated "to contain" or "to deliver" a definite volume of liquid. This will be indicated on the apparatus with the letters "TC" (to contain) or "TD" (to deliver). Volumetric flasks are calibrated to contain a given volume. They are available in various shapes and sizes ranging from 1 to 2000 ml capacity.

Volumetric pipets are calibrated to deliver a fixed volume. The usual capacities are 1 to 100 ml although micro-pipets are also available. In emptying volumetric pipets, they should be held in a vertical position and the outflow should be unrestricted. The tip of the pipet is kept in contact with the wall of the receiving vessel for a second or two after the free flow has stopped. **The liquid remaining in the tip is not removed,** this is most important.

Measuring and serological pipets should also be held in a vertical position for dispensing liquids; however, the tip of the pipet is only touched to the wet surface of the receiving vessel after the outflow has ceased. For those pipets where the small amount of liquid remaining in the tip is to be blown out and added, indication is made by a frosted band near the top. The band is usually located far enough down so that it will not touch the technician's lips when liquid is being drawn up or blown out.

Burets are used to deliver definite volumes. The more common types are usually of 25- or 50-ml capacity, graduated to tenths of a milliliter, and are provided with stopcocks. For precise analytical methods in microchemistry, micro-burets are also used. Micro-

burets generally are of 5- or 10-ml capacity, graduated in hundredths of a milliliter division. Automatic burets with reservoirs are also available ranging in capacity from 10 to 100 ml. Reservoir capacity ranges from 100 to 4000 ml.

General rules in regard to the manipulation of a buret are as follows:

- Do not attempt to dry a buret which has been cleaned for use, but rinse it two or three times with a small volume of the solution with which it is to be filled.
- Do not allow alkaline solutions to stand in a buret, because the glass will be attacked, and the stopcock, unless made of Teflon, will tend to freeze.
- A 50-ml buret should not be emptied faster than 0.7 ml per second, otherwise too much liquid will adhere to the walls and as the solution drains down, the meniscus will gradually rise, giving a high false reading.
- It should be emphasized that improper use of and/or reading of burets can result in serious calculation errors.

In the case of all apparatus for delivering liquids, the glass must be absolutely clean so that the film of liquid never breaks at any point. Careful attention must be paid to this fact or the required amount of solution will not be delivered. The various cleaning agents and their use are described later.

4.3.2.1 Specifications for Volumetric Glassware

Several standards, such as DIN, NBS, etc., describe the specifications for volumetric glassware. In general, volumetric glass apparatus, which meet standard specifications are designated as Class A and all such glassware is permanently marked with a large "A". In addition to the "A" marking found on calibrated glassware and the temperature at which the calibration was made, other markings also appear. These include the type of glass, such as Pyrex, etc., the stock number of the particular item, and the capacity of the vessel. According to the DIN standard, the tolerance is also marked, such as 25 ml ± 0.030 ml.

4.3.3 Cleaning of Glass and Porcelain

The method of cleaning should be adapted to both the substances that are to be removed, and the determination to be performed. Water-soluble substances are simply washed out with hot or cold water, and the vessel is finally rinsed with successive small amounts of distilled water. Other substances more difficult to remove may require the use of a detergent, organic solvent, dichromate cleaning solution, nitric acid or aqua regia (25 percent v/v conc. $HN0_3$ in conc. HCl). In all cases it is good practice to rinse a vessel with tap water as soon as possible after use. Material allowed to dry on glassware is much more difficult to remove.

Volumetric glassware, especially burets, may be thoroughly cleaned by a mixture containing the following: 30 g sodium hydroxide, 4 g sodium hexametaphosphate (trade name, Calgon), 8 g trisodium-phosphate, and 1 litre water. A gram or two of sodium laurylsulphate or other surfactant will improve its action in some cases. This solution should be used with a buret brush.

4.3.3.1 Special Cleaning Requirements

Absorption cells, used in spectrophotometers, should be kept scrupulously clean, free of scratches, fingerprints, smudges and evaporated film residues. The cells may be cleaned with detergent solutions for removal of organic residues, but should not be soaked for prolonged periods in caustic solutions because of the possibility of etching. Organic solvents may be used to rinse cells in which organic materials have been used. Nitric acid rinses are permissible, but dichromate solutions are not recommended because of the adsorptive properties of dichromate on glass. Rinsing and drying of cells with alcohol or acetone before storage is a preferred practice. Matched cells should be checked to see that they are equivalent by placing portions of the same solution in both cells and taking several readings of the transmittance (%T or optical density (OD) values. If a cell is mismatched it should be discarded or reserved for rough work.

For certain determinations, especially trace metals, the glassware should also be rinsed with a 1:1 nitric acid-water mixture. This operation is followed by thoroughly rinsing with tap water and successive portions of distilled water. This may require as many as 12-15 rinses, especially if chromium is being determined. The nitric acid rinse is also especially important if lead is being determined.

Glassware to be used for phosphate determinations should not be washed with detergents containing phosphates. This glassware must be thoroughly rinsed with tap water and distilled water. For ammonia and Kjeldahl nitrogen, the glassware must be rinsed with ammonia-free water.

Glassware to be used in the determination of trace organic constituents in water, such as chlorinated pesticides, should be as free as possible of organic contaminants. A chromic acid wash of at least 15 minutes is necessary to destroy these organic residues. Rinse thoroughly with tap water, and finally with distilled water. Glassware may be dried for immediate use by rinsing with redistilled acetone. Otherwise glassware may be oven dried or drip-dried. Glassware should be stored immediately after drying to prevent any accumulation of dust. Store inverted or with mouth of glassware covered with foil.

Bottles to be used for the collection of samples for organic analyses should be rinsed successively with chromic acid cleaning solution, tap water, distilled water, and finally several times with redistilled solvent (e.g., acetone, hexane, petroleum ether, chloroform).

Caps are washed with detergent, rinsed with tap water, distilled water and solvent. Liners are treated in the same way as the bottles and are stored in a sealed container.

4.3.4 Disposable Glassware

When the risk of washing a pipet for reuse becomes too great, as in the case of use with toxic materials, or when the cost of washing glassware becomes prohibitive, disposable pipets may be the answer, provided they meet the necessary specification. Various types are available including bacteriological, serological and micro-dilution pipets. Disposable glassware generally is made of soft glass.

4.3.5 Specialized Glassware

The use of vessels and glassware fitted with standard-taper, ground-glass, and ball-and-socket joints has increased because of certain advantages such as less leakage, etc. Standard-taper, interchangeable ground joints save time and trouble in assembling apparatus. They are tested precision-ground to insure an accurate fit and freedom from leakage. Ball and socket joints increase flexibility of operation and eliminate the need for exact alignments of apparatus.

4.4 Reagents, Solvents and Gases

The objective of this chapter is to provide general information and suggestions that will serve to keep the analyst conscious of his responsibilities in analytical quality control, as they relate to reagents, solvents and gases. While the material presented here will assist the analyst in producing high quality data, it is by no means complete. It is incumbent on the analyst to obtain details of special precautions required to insure proper selection, preparation, and storage of reagents, solvents and gases from the descriptions of individual methods. It is required that the date of preparation and expiery be shown on the storage bottle. Each bottle should be labeled showing its content, date of preparation and the name of the analyst.

4.4.1 Reagent Quality

Chemical reagents, solvents, and gases are available in a wide variety of grades of purity, ranging from technical grade to various "ultra pure" grades. The purity of these materials required in analytical chemistry varies with the type of analysis. The parameter being measured and the sensitivity and specificity of the detection system are important factors in determining the purity of the reagents required. For many analyses, e.g., most inorganic analyses, analytical reagent grade is satisfactory. Other analyses, e.g., trace organic and radiological, frequently require special "ultra pure" reagents, solvents, and gases. In methods where the purity of reagents is not specified it is intended that analytical reagent grade be used. Reagents of lesser purity than that specified by the method should not be used. The labels on the container should be checked and the contents examined to verify that the purity of the reagents meets the needs of the particular method involved. The quality of reagents, solvents, and gases required for the various classes of analyses: inorganic, metals, radiological, and organic, are discussed below.

Reagents must always be prepared and standardised with care and appropriate technique against reliable primary standards. They must be re-standardised or prepared fresh as often as required by their stability. Stock and working standard solutions must be checked regularly for signs of deterioration, e.g., discoloration, formation of precipitates, and concentration. Standard solutions should be properly labeled as to compound, concentration, solvent, date and prepared.

Primary standards must be obtained from a reliable source, pretreated, e.g., dried, under specified conditions, accurately prepared in calibrated volumetric glassware, and stored in containers that will not alter the reagent. A large number of primary standards, certified reference materials (CRM) are available from the different suppliers (NBS, etc.).

Primary standards may also be obtained from many chemical supply companies. Suppliers for special quality reagents, solvents, and gases are noted in later discussions of the various classes of analyses. Reagents and solvents of all grades are available from many chemical suppliers.

There is some confusion among chemists as to the definition of the terms ANALYTICAL REAGENT GRADE, REAGENT GRADE, and ACS ANALYTICAL REAGENT GRADE. In this document, the term ANALYTICAL REAGENT GRADE (AR) will be used. It is intended that AR chemicals and solvents shall conform to the current specifications set up by competent committees, advisory groups.

The type of volumetric glassware to be used, the effect of certain reagents on glassware, the effect of temperature on volumetric measurements, purity of reagents, absorption of gases and water vapour from the air, standardization of solutions, instability, and need for frequent standardisation of certain reagents are among the factors to be considered and described in the literature. It is recommended that the analyst become thoroughly familiar with the relevant publications.

4.4.2 General Inorganic Analyses

In general, AR-grade reagents and solvents are satisfactory for inorganic analyses. Primary standard reagents must, of course, be used for standardizing all volumetric solutions. Commercially prepared reagents and standard solutions are very convenient and may be used when it is demonstrated that they meet the method requirements. All prepared reagents must be checked for accuracy.

The individual methods specify the reagents that require frequent standardization, or other special treatment, and the analyst must follow through with these essential operations. To avoid waste, the analyst should prepare a limited volume of such reagents, depending on the quantity required over a given period of time.

As far as possible, distilled water used for preparation of reagent solutions must be free of measurable amounts of the constituent to be determined. Special requirements for distilled water are given in Section 3.1.1 of this guidance and in individual method descriptions.

Compressed gases, such as oxygen and nitrogen, used for total organic carbon determination may be of commercial grade.

4.4.2.1 Analyses of Metals

All standards used for atomic absorption and emission spectroscopy should be of spectroquality. It is recommended that other reagents and solvents also be of spectroqualiiy, although AR grade is sometimes satisfactory. Standards may be prepared by the analyst in the laboratory or prepared, spectrographically standardised materials may be purchased commercially. Multielement standard solutions are also available.

Analytical reagent grade nitric and hydrochloric acids must be specially prepared by distillation in borosilicate glass and diluted with deionised distilled water. All other reagents and standards are also prepared in deionised water.

In general, fuel and oxidant gases used for atomic absorption can be of commercial grade. Air supplied by an ordinary laboratory compressor is quite satisfactory, if adequate pressure is maintained and necessary precautions are taken to filter oil, water, and possible trace metals from the line. For certain determinations, e.g., aluminum, reagent-grade nitrous oxide is required; for analysis of mercury suprapure acid is needed.

4.4.3 Radiological Analyses

The great sensitivity of radioactive counting instruments requires that scintillation grade reagents and solvents, or equivalent, be used for all radioactivity determinations. Some of the reagents, for example, strontium carbonate and yttrium oxide carriers used for the determination of strontium 90 and yttrium 90, must be stable, that is free of radioactivity. Barium sulphate, used for co-precipitation of radium must be free from all traces of radium. These reagents and solvents are commercially available from chemical supply houses. Calibrated standard sources of specific radioactive materials with known count and date of counting are available from various suppliers. No single company supplies all standards.

Gases used for radioactive counting must be of high purity and extra dry. Gases such as helium and air are aged for about 30 days to allow radioactive background to decay. All gases are checked for background before use. Some cylinders contain inherent radioactivity which is imparted to the gas. When this background is above normal, the gas should not be used for radioactivity determinations.

4.4.4 Analyses of Organic Compounds

The minimum purity of reagents and solvents that can be used for organic analyses is AR grade. Reference grade standards should be used whenever available. Special note should be taken of the assay of standard materials. Owing to the great sensitivity (nanogram and sub-nanogram quantities) of gas chromatography (GC), which is often used to quantitate organic results, much greater purify is frequently required. The specificity of some GC detectors requires that reagents and solvents be free of certain classes of compounds. For example, analyses by electron capture require that reagents and solvents be free of electronegative materials that would interfere with the determination of specific compounds in the sample. Similarly, use of the flame photometric detector requires that reagents and solvents be free from sulphur and/or phosphorus interference. Pesticide quality solvents are available from several sources. These are often satisfactory for many organic GC determinations. However, the contents of each container must be checked to assure its suitability for the analyses. Similarly, all analytical reagents and other chemicals must also be checked routinely.

The quality of gases required for GC determinations varies somewhat with the type of detector. In general, the compressed gases are a pre-purified dry grade. The nitrogen-detection system requires the use of ultra-pure hydrogen for satisfactory results. The

use of molecular-sieve, carrier-gas filters and drying tubes is required on combustion gases. They are recommended for use on all other gases.

Adsorbents most commonly used for column chromatographic clean-up of sample extracts are Florisil, silica gel, and alumina. These must be pre-activated according to the method specifications and checked for interfering constituents.

4.4.5 Storing and Maintaining Quality of Reagents and Solvents

Having carried out the tasks of selecting, preparing, and verifying the suitability of reagents, solvents, and gases, the analyst must properly store them to prevent contamination and deterioration prior to their use. Borosilicate glass bottles with ground glass stoppers are recommended for most standard solutions and solvents. Plastic containers, e.g., polyethylene, are recommended for alkaline solutions. Plastic containers must not be used for reagents or solvents intended for organic analyses. However, plastic containers may be used for reagents not involved with organic analyses if they maintain a constant volume, and it is demonstrated that they do not produce interferences and do not absorb constituents of interest. It is important that all containers be properly cleaned and stored prior to use.

Standard reagents and solvents must always be stored according to the manufacturer's directions. Reagents or solvents that are sensitive to the light should be stored in dark bottles and/or stored in a cool, dark place. It is particularly important to store materials used for radiological determinations in dark bottles, since photoluminescence will produce high background if light sensitive detectors are used for counting. Some reagents require refrigeration.

Adsorbents for column chromatography are stored in the containers that they are supplied in, or according to the requirements of individual methods. Activated carbon, used for collection of samples for organic analyses, must be stored and processed in areas protected from atmospheric and other sources of contamination.

The analyst should pay particular attention to the stability of the standard reagents. Standards should not be kept longer than recommended by the manufacturer, or in the method. Some standards are susceptible to changes in normality due to absorption of gases or water vapour from the air.

The concentration of the standards will change as a result of evaporation of solvent. This is especially true of standards prepared in volatile organic solvents. Therefore, the reagent bottles should be kept stoppered, except when actually in use. The amount of evaporated solvent can be checked by weighing the closed bottle after and before using. The amount of the evaporated solvent should be added to the solution before its use. The chemical composition of certain standards may change on standing. Certain pesticides, for instance, will degrade if prepared in acetone that contains small quantities of water. Thus, it is essential that working standards be frequently checked to determine changes in concentration or composition. Stock solutions should be checked before preparing new working standards from them.

4.5 Elimination of Determinate Errors

In order to produce high quality analytical data, determinate errors must be eliminated or at least minimised. For this purposes, we assume that a competent analyst and reliable equipment, in optimum operating condition, are available. Thus, determinate errors that might result from an inexperienced or careless analyst and poor equipment are eliminated. The remaining sources of error are the reagents, solvents, and gases that are used throughout the analyses. The quality of these materials, even though they are AR grade or better, may vary from one source to another, from one lot to another, and even within the same lot. Therefore, the analyst must predetermine that all of these materials are free of interfering substances under the conditions of the analyses. To do this she/he must have a regular check program. Materials that do not meet requirements should be replaced or purified so that they can be used.

4.5.1 Reagent Blank

The first step the analyst must take is to determine the background or blank of each of the reagents and solvents used in a given method of analysis. The conditions for determining the blank must be identical to those used throughout the analysis, including the detection system. If the reagents and solvents contain substances that interfere with a particular determination, satisfactory reagents and solvents must be found. Where possible and practical, they should be treated so that they can be used.

4.5.2 Method Blank

After determining the individual reagent or solvent blanks, the analyst must determine the method blank to see if the cumulative blank interferes with the analyses. The method blank is determined by following the procedure step by step, including all of the reagents and solvents, in the quantity required by the method. If the cumulative blank interferes with the determination, steps must be taken to eliminate or reduce the interference to a level that will permit this combination of solvents and reagents to be used. If the blank cannot be eliminated, the magnitude of the interference must be considered when calculating the concentration of specific constituents in the samples being analysed.

A method blank should be determined whenever an analysis is made. The number of blanks to be run is determined by the method of analysis and the number of samples being analysed at a given time. In some methods, the method blank is automatically and continuously compensated for since a continuous flow of the reagents passes through the detector. In other procedures, such as the gas chromatographic determination of pesticides, a method blank is run with each series of samples analysed. Usually this is one blank for every nine samples.

4.5.3 Elimination of Interferences

Procedures for eliminating or at least minimising impurities that produce specific interferences or high general background, vary with the reagent and method involved. These procedures may include: re-crystallization, precipitation, distillation, washing with an appropriate solvent, or a combination of these. Examples of procedures used for

various types of analyses are given below. For complete information, the analyst should consult the individual methods.

4.5.3.1 General Inorganic Analysis

Analytical reagent grade chemicals and solvents usually present no interference problems in inorganic analyses. However, some reagents do not always meet methods requirements. An example is potassium persulfate used in phosphorus and nitrogen determinations. This reagent is frequently contaminated with ammonia. Therefore, it is routinely purified by passing air through a heated water solution of the reagent. The purified potassium persulfate is recovered by re-crystallization.

A problem more commonly encountered in inorganic analyses is the rapid deterioration of the standard reagents and other ingredients. To minimize or eliminate this problem some reagents, for example, ferrous ammonium sulphate, must be standardized daily. Others, such as sodium thiosulphate used for dissolved oxygen determination, may require a substitute reagent, e.g., phenyl-arsenic-oxide. Solid phenol, which readily oxidizes and acquires a reddish colour can be purified by distillation. Starch indicator used for idiometric titrations may be prepared for each use or preserved by refrigeration, or by addition of zinc chloride or other suitable compounds.

4.5.3.2 Metal Analysis

In general, spectrograde chemicals, solvents, and gases present no interference problems in atomic absorption or emission spectrographic determinations. However, standards, which do not meet the requirements of the method are sometimes obtained. Ordinarily, no effort is made to purify them. They are simply replaced by new reagents of sufficient purity. Some reagents may form precipitates on standing. Such reagents will reduce the accuracy of quantitative analyses and should not be used.

4.5.3.3 Radiological Analysis

In general, reagents that do not meet the purity requirements for radiological determinations are replaced with reagents that are satisfactory. However, in some instances (for example, barium sulphate used for co-precipitation of radium), it may be necessary to carry out repeated re-crystallization to remove all forms of radium, and reduce the background count to a useable level. In some instances, solvents that do not meet requirements may be distilled to produce adequate purity. In some cases, gases having background counts may be useable after aging as described earlier. If not, they should be replaced with gases that are satisfactory.

4.5.3.4 Organic Analysis

Many AR-grade chemicals and solvents, and at times pesticide quality solvents, do not meet the specifications required for the determination of specific organic compounds. Impurities that are considered trace, or insignificant, for many analytical uses are often present in greater quantities than the organic constituents being measured. Coupled with the several-hundred-fold concentration of the sample extract that is usually

required, such impurities can cause very significant interferences in trace organic analyses.
Reagents and solvents found to be unsatisfactory, under the conditions of the analyses, must be replaced or cleaned up so that they are useable. Some useful clean-up procedures are:

- Washing the inorganic reagents with each solvent that the reagent contacts during the analysis,
- Washing the adsorbents, such as silica gel G and Florisil, with the solvents that are used for a specified column or thin-layer chromatographic procedure,
- Pre-extracting distilled water with solvents used for the particular analysis involved,
- Pre-extracting aqueous reagent solutions with the solvents involved,
- Redistilling solvents in all-glass systems using an efficient fractlonating column,
- Re-crystallizing reagents and dyes used in colorimetric or thin-layer determinations,

If the reagents and solvents thus produced are not of sufficient purity, they should be replaced.

Dirty gases (quality less than specified) are particularly troublesome in gas chromatographic analyses. They may reduce the sensitivity of the detector, and produce a high or noisy baseline. If this occurs, the cylinder should be replaced immediately. Similarly, if cylinders of compressed gases are completely emptied in use, the end volumes of the gas may produce a similar and often more severe effect. Oils and water may get into the system and foul the defector. When this occurs the system must be dismantled and cleaned. Overhaul of the detector may be required. To reduce chances of this, it is recommended that all gas cylinders be replaced when the pressure falls to 100-200 psi. Filter driers are of little help in coping with this type of contamination.

4.6 Laboratory supplies

To provide some orientation for the user of this guidance, laboratory supplies needed for a general water chemical laboratory, for trace inorganic and trace organic laboratory are summarised in Annex 3.

5 SPECIAL REQUIREMENTS FOR TRACE ORGANIC ANALYSIS

The high sensitivity of the instrumentation used in trace organic chemical analysis, and the low concentration of compounds being investigated, dictate that special attention be given this field of analytical endeavor. Contamination of the sample from any possible source must be diligently guarded against, and interferences in the sample must be carefully controlled. Finally, strict attention to method and highly refined technique are required to produce valid quantitative results.

5.1 Collection of the Samples

5.1.1 Discrete Bottled Samples

Sample collection should be done with wide-mouth glass bottles, equipped with screw caps fitted with Teflon liners. The use of a screw cap without a Teflon liner may cause contamination of the sample by the liner or adhesive used in sealing the liner to the cap. Plastic bottles (polyethylene) are not used because traces of plasticizer may be leached from the plastic by the water, and can be a source of analytical interference. Moreover, organics from the sample may be adsorbed on the plastic. It has been suggested that high grade Teflon bottles may be satisfactory for this use, however, the cost is prohibitive at present.

To insure freedom from organic contaminants, bottles are rinsed successively with chromate cleaning solution, running tap water, distilled water, and finally several times with redistilled solvent (e.g., acetone, hexane, petroleum ether, chloroform). Caps are washed with detergent, rinsed with tap water, distilled water, and solvent. Liners are treated in the same way as the bottles and are stored in a sealed container.

Each method designates a recommended sample size for surface water analysis. Duplicate samples are recommended. If analysis by more than one method is to be requested on the same sample, sufficient sample must be simultaneously obtained to supply the needs of each analysis.

It is also recommended that when requesting a non-specific analysis, any information that could help direct the analytical approach, or aid in interpretation of results, be supplied. Such information could include industrial or agricultural activities in the area from which the sample was obtained, spills, or other accidents that may have occurred in the area. Also mention of similar upstream activity could provide valuable assistance.

Samples should be stored in a cool, dark place, and analysed as soon as possible. If the sample cannot be analysed immediately, reporting the holding time can help in interpreting results where die-off rates are known.

5.1.2 Carbon Adsorption Samples

The affinity of the activated carbon for organic substances requires that supplies of carbon be protected from extraneous sources of contamination. For example, carbon can adsorb organic substances from the air. Therefore, the activated carbon is stored and processed in an area adequately protected from such sources of contamination. As an additional precaution, the ventilating, heating, and air conditioning systems for the laboratories in which carbon adsorption samples are processed should be completely isolated from all other laboratories.

5.2 Glassware

Proper calibration of volumetric glassware is essential to valid analytical results, because quantitation is performed by comparison to measured amounts of standard compounds, and by accurate measurement of sample volume.

Individual concentrator tubes, used to measure final concentrate volumes, must first be calibrated at the working volume. This is particularly important for volumes less than 1 ml. Calibration should be made by noting the number of microliters of solvent required to bring the liquid level (lower meniscus) up to a particular graduation mark. A precision 100 µl syringe should be used to measure calibration volume. Volumes can also be determined by weighing.

It is also very important in trace organic analysis that glassware be as free as possible of any organic contaminants. A strong acid cleaning solution is required for removing all traces of organic material from glassware. Heating of the glassware (200 ^{o}C, > 2h) can be an option, but volumetric glassware is not reliable after that.

5.3 Reagents and Chemicals

The minimum purity of reagents and chemicals should be certified (analytical reagent) grade. Analytical standards should be reference grade, when available. The analyst should take special note of the assay of less pure materials (most often pesticides). All reagents and chemicals should be stored according to manufacturer's instructions to prevent degradation. Proper storage is especially important if the chemical is to be used in preparing an analytical standard. Refrigerated chemicals should be allowed to come to room temperature before exposing them to the atmosphere.

When preparing stock solutions, it is recommended that at least 10 mg of material be used for greater accuracy in weighing. Solutions should be carefully stored so as to preserve their concentration, and to protect them from ultraviolet radiation. Usually storage in ground-glass stoppered bottles, either amber-glass or out of the line of direct lighting, is sufficient.

Standard solutions should be prepared using precision syringes to measure the volume of stock solution to be diluted. The syringe barrel should be pre-wetted with solvent and air bubbles expelled. Dilution should be done in a Class A volumetric flask to insure accurate measurement. If these solutions are to be used frequently, they are best stored in a screw-cap, septum, sealed vial. These vials allow instant access to the solution and offer good protection against concentration changes of the standard solution.

Evaporation of the solvent caused by repeated removal of the cap is a serious problem with other containers. If septum vials are not available it is advisable to prepare standard solutions in a volumetric container of 100 ml or more and transfer a small portion to a separate container for daily use, then discard that portion at the end of the day.

All stock or standard solutions should be carefully watched fox signs of changes in concentration or deterioration. As an aid to monitoring these solutions, it is wise to label them as to compound, concentration, solvent used, date and prepared. Also, in the case of GC solutions, it is necessary to retain some evidence of its chromatographic behavior as a fresh solution for comparison at a later date.

Distilled water used as dosed, control samples must be free of organic interferences. A very effective way of removing organic interferences from distilled water is to pre-extract the water with the solvent that is to be used in the analysis, then boil the water to remove the residual solvent.

Organic solvents used in pesticide analysis should be pesticide quality, and demonstrated to be free of interferences in a manner compatible with whatever analytical operation is to be performed. Solvents can be checked by analysing a volume equivalent to that used in the analysis and concentrated to the minimum final volume. Possible interferences are noted in terms of factors such as relative retention times, peak geometry, peak intensity, and width of solvent response. Interferences noted under these conditions can be considered maximum. If necessary, a solvent must be redistilled in glass using a 60-cm column packed with 1/8" glass helices, or an equivalent system.

Hexane-ethyl ether and benzene are commonly used in the extraction of water and wastewater in conjunction with analysis by electron-capture gas-liquid chromatography. Because electron-capture detection methods are extremely sensitive to interferences normally found in these solvents, the cleanest possible reagent grade or pesticide quality solvents must be used. Redistillation in the lab in an all-glass system might be necessary. Solvents in the same lot may also vary and therefore each container should be checked.

5.4 Common Analytical Operations

Adequate steps must be taken to eliminate or minimize interferences from solvents and other materials. A blank should be run simultaneously under the same analytical conditions as any block of samples analysed. A block of samples is defined as any group of one or more samples analysed using a common batch of analytical supplies. Should any one of the supplies be changed (i.e., solvent, silica gel, Florisil, etc.) a new blank is required.

Quantitation of micro amounts of organic materials requires extremely careful technique to avoid loss of sample. Quantitative transfers are essential to obtain accurate and precise results. Practice in these manipulations is recommended for the inexperienced analyst.

Concentration of sample extracts to very small volumes for trace analysis requires great care to avoid loss of constituents. A Kuderna-Danish evaporator is a very useful apparatus to accomplish this operation. Instructions in the use of this evaporator must be strictly followed to avoid loss of desired sample. Final concentration in an ampoule or calibrated tube is accomplished in a warm water bath with a gentle stream of clean, dry air, if air oxidation is not a problem; otherwise, nitrogen should be used. During the final concentration, the inside walls should be rinsed repeatedly with the working solvent to insure the total sample is contained in the bottom of the tube. Complete evaporation of solvent must be avoided to prevent loss of sample constituents. The step should be accomplished within 10 or 12 minutes for best results.

6 CONTROL OF ANALYTICAL PERFORMANCE

It is assumed that a valid sample has been properly taken, preserved, and delivered to the laboratory for analyses; that the laboratory analyses were done according to recognised, standardised methods; and that the recording and reporting of subsequent laboratory results were done in a systematic and uniform way. It must be recognised and practiced, however, that quality control begins with the sample collection and does not end until the resulting data are reported. The laboratory control of analytical performance is one vital link in obtaining valid data, however, use of quality control between field sampling, laboratory analyses and management decisions are necessary to insure this validity.

Earlier we have discussed such key elements as laboratory services, instrumentation, glassware, reagents, solvents, and gases, therefore, we should refer to these sections to determine the necessary specifications and requirements required for quality control. On the assumption that these variables are under control, that a single method is being used, and that the complete system is initially under control, what should be done in the evaluation of daily performance to document that valid data are being produced? First, valid precision and accuracy data should be available on the method. Thereafter, systematic daily checks (e.g., analysing blanks, calibration standards, quality control check samples, reference materials) are required to show that reproducible results are being obtained and that the methodology is actually measuring what is in the sample. These items are discussed in detail in the following sections.

6.1 Precision and Accuracy

Precision refers to the reproducibility among replicate observations. In an AQC programme it is determined by the use of actual water samples, which cover a range of concentrations and a variety of interfering materials usually encountered by the analyst. Obviously, such data should not be collected until the analyst is thoroughly familiar with the method, and has obtained a reproducible standard curve. For colorimetric analyses, the initial standard curve should include a blank and a series of at preferably eight standards encompassing the full concentration range to be used for routine sample analyses. Subsequently, at least two standards (a high and a low) should be analysed to verify the original standard curve. For other measurements, such as pH, conductivity, etc., instruments should be standardised according to manufacturer's instructions and sound, scientific practice.

There are a number of different methods available for the determination of precision. One method that can be successfully employed, and can be adapted to several analytical instrumentation and chemical procedures, is described as follows:

- Four separate concentration levels should be studied, including a low concentration near the sensitivity level of the method, two intermediate concentrations, and a concentration near the upper limit of application of the method.
- Seven replicate determinations should be made at each of the concentrations tested.

- To allow for changes in instrument conditions, the precision study should cover at least two hours of normal laboratory operation.
- In order to permit the maximum interferences in sequential operation, it is suggested that the samples be run in the following order: high, low, intermediate, intermediate. This series is then repeated seven times to obtain the desired replication.
- The precision statement should include a range of standard deviations over the tested range of concentration. Thus, four standard deviations will be obtained over a range of four concentrations, but the statement should contain only the extremes of standard deviations and concentrations studied.

An example of data generated from such an approach is shown in Table 15.

Table 15. Precision data on river water samples for PO_4-P, in mg P/l.

Sample	Danube	Tisa	Sio	Sajo
1	0.05	0.10	0.48	0.62
2	0.06	0.10	0.48	0.62
3	0.06	0.10	0.49	0.62
4	0.06	0.11	0.48	0.63
5	0.06	0.11	0.48	0.62
6	0.06	0.11	0.48	0.62
7	0.06	-	-	0.62
Average	0.059	0.105	0.482	0.621
s	0.004	0.005	0.004	0.004

The resulting precision statement would read as follows:

> "In a single laboratory, using surface water samples at concentrations of 0.06, and 0.62 mg P/l, the standard deviation was ±0.004”

Thus, the statement contains the number of laboratories involved, the type of samples, the concentrations used and the resulting standard deviation (s).

Accuracy refers to a degree of difference between observed and known, or actual, values. Again, accuracy should be determined on actual water samples routinely analyzed, and preferably, on the same series as those used in the precision determinations. The method employed consists of the following key steps:

- Known amounts of the particular constituent should be added to actual samples at concentrations where the precision of the method is satisfactory. It is suggested that amounts be added to the low-concentration sample, sufficient to double that concentration, and that an amount be added to one of the intermediate concentrations, sufficient to bring the final concentration in the sample to approximately 75% of the upper limit of application of the method.
- Seven replicate determinations at each concentration should be made.

- Accuracy should be reported as the percent recovery at the final concentration of the spiked sample. Percent recovery at each concentration should be the mean of the seven replicate results.
- Data were obtained with this approach by using two of the water samples previously used in the precision study reported in Table 15. (Danube and Sio rivers). They are reported in Table 16.

Table 16. Accuracy data on river water samples for PO_4-P, in mg P/l.

Sample	**Danube** (Added 0.06 mg P/l)	**Sio** (Added 0.3 mg P/l)
1	0.105	0.74
2	0.105	0.75
3	0.105	0.75
4	0.110	0.73
5	0.110	0.74
6	0.110	0.75
7	0.105	0.75
Average	0.107	0.74

Again, in order to contain the key elements, the accuracy statement would read as follows:

"In a single laboratory, using surface water samples at concentrations of 0.11 and 0.74 mg P/l, recoveries were 90% and 95%, respectively".

Once collected and documented, these precision and accuracy data may be used in a number of ways. Two important examples are:

(2) They present evidence that the analyst in question is indeed capable of analysing the water samples for that particular parameter. That is, he has the standard method under control, and is capable of generating valid data, and

(3) The data can be used in the evaluation of daily performance in reference to replicate samples, spiked standards and samples, and in the preparation of quality control charts.

The above methods can be adapted to other chemical procedures and analytical instruments. They can be used on manual titration methods for such parameters as alkalinity, chloride, and hardness; on general inorganic instruments such as pH, conductivity; on TOC and AOX instruments, etc. Other instruments, such as atomic absorption and flame emission spectrophotometers could also be evaluated by these methods, however, radiological instrumentation and gas chromatography systems require special techniques.

6.2 Evaluation of Daily Performance

Once valid precision and accuracy data are available on the method, systematic daily checks are necessary to insure that valid data are being generated. First of all, verification of the originally-constructed standard curve is mandatory. As previously noted, at least two standards (a high and a low) should be analysed routinely along with a blank to determine that comparable operating conditions exist. If the data do not substantiate such control, the analyst must systematically trouble-shoot his system until the problem is corrected.

In order to document that reproducible results are being obtained (i.e., precision of the method), it is necessary to run replicate samples. Although frequency of such replicate analyses is, by nature, dependent on such factors as the original precision of the method, the reliability of the instrumentation involved, and the experience of the analyst, good laboratory technique is to run duplicate analyses at least ten percent of the time. The resulting data should agree favorably with the known precision of the method. If they do not, the system is not under control, and results are subject to question.

Concurrently, quality control should include assurance that the daily system is actually measuring what is in the sample (i.e., accuracy of the method). Although it is far preferable to have obtained values check with known or actual values, it should be recognized that inaccuracy does not destroy the value of data if the degree and precision of the error is known and taken into account. In order to account for background contamination and/or sample interferences, and as a matter of routine practice, spiked samples should be used in addition to standards. As in the case of duplicate sample analyses, good laboratory technique dictates that spiked samples be run at least ten percent of the time.

Thus, daily control of analytical performance in the laboratory requires approximately 5-20 percent of the analyst's time. Considering the elapsed time and combined efforts of skilled personnel that are represented in a final laboratory result, this is a comparatively small price to pay for, not a ”number", but a valid concentration value.

A most convenient way of recording the obtained precision and accuracy data is through the preparation of quality control charts. Plotting of said data systematically answers the question as to whether the laboratory analyses are under control, and is useful in observing developing trends of positive or negative bias. Because of its importance in documenting the quality control being practiced daily in the laboratory, the construction and uses of quality control charts are treated as a separate topic in the next section.

A broader and somewhat different form of evaluation of daily performance may be made through routine participation in interlaboratory round-robin studies. Samples analysed in such a cooperative program should be treated as part of the routine sample load. In so doing, the analyst is able to compare his individual performance against other laboratory personnel, and to have a reliable measure of the particular method's capabilities. In many respects such samples can be regarded as reputable "blind samples"; a necessary ingredient in the quality control of laboratory results.

6.2.1 Quality Control Charts

Quality control charts were originally developed for the control of production processes where large numbers of items were being manufactured and inspected on an essentially continuous basis. As shown in Fig. 3., a control chart consists of a graphical chart with the vertical scale plotted in units of the test result, or recovery, and the horizontal scale in units of time or sequence of results. The upper and lower warning and control limits shown on the chart are used as criteria for action, or for judging the significance of variations between duplicate samples. The central line represents the average or the standard value of the statistical measure being plotted.

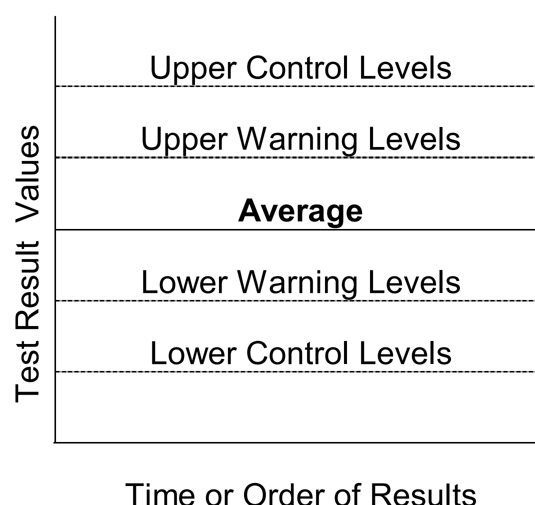

Fig. 3. Essentials of the accuracy chart

As observed in the previous section on the evaluation of daily performance, daily precision and accuracy data can be plotted by means of these quality control charts to determine if valid, questionable, or invalid data are being generated from day to day. There are several techniques available for actually constructing quality control charts and plotting subsequent data. Two types of control charts are commonly used in laboratories: (1) accuracy or means charts for QC samples are constructed from reagents blanks, laboratory control standards, calibration check standards, laboratory fortified blanks, laboratory fortified matrices and surrogates, and (2) precision or range charts are % relative standard deviation (RSD) or relative percent difference (RPD) for replicate or duplicate analyses. These charts are essential tools for quality control.

The accuracy chart for QC samples is from the average and standard deviation of a specified number of measurements of the analyte of interest. The accuracy chartincludes upper and lower warning (WL) and control levels (CL). Common practice is to use $\pm 2s$ and $\pm 3s$ limits for the WL and CL, respectively. These values are derived from results from analysis of reference materials. The number of measurements to calculate standard deviation should be relevant to the statistical confidence limits of 95% for the WLs and 99% for the CLs. Percent recovery can be used in the case of samples if the concentration varies.

The precision chart is also constructed from the average and standard deviation of a specified number of measurements of the analyte of interest. If teh standard deviation of the method is known the factors given in the following can be used to constuct the central line and the warning and control limits:

Number of Observations n	Factor for Central Line D_2	Factor for Control Lines D_4
2	1.128	3.267
3	1.693	2.575
4	2.059	2.282
5	2.326	2.115

In the precision chart, only upper warning and control limits are meaningful. The standard deviation is converted to the range so that the analyst need only subtract the two results to plot the value on the precision chart. The mean range is computed as:

$$\bar{R} = D_2 s$$

the control limit as

$$CL = \bar{R} \pm 3s(R) = D_4 \bar{R}$$

and the warning limit as

$$WL = \bar{R} \pm 2s(R) = \bar{R} \pm 2/3(D_4 \bar{R} - \bar{R})$$

where
D_2 = factor to convert s to the range (1.128 for duplicates, as above),
$s(R)$ = standard deviation of the range,
D_4 = factor to convert mean range to $3s(R)$ (3.267 for duplicates, as above).

A precision chart is very simple when duplicate analyses of a standard are used.

To start with a quality control chart it is a practical way to measure seven times a check solution with a concentration level between 40 to 60% of the range. Calculate the mean and the standard deviation, and follow the preparation of the control chart as mentioned above.

7 DATA HANDLING AND REPORTING

To obtain meaningful data on water quality, the laboratory must first collect a representative sample and deliver it unchanged for analysis. The analyst must then complete the proper analysis in the prescribed fashion. Having accomplished these steps, one other important step must be completed before the data are of use. This step includes the permanent recording of the analytical data in meaningful exact terms, and reporting it in proper form to some storage facility for future interpretation and use.

It is very important that starting from the sampling through the laboratory work until reporting the results, the name of the responsible person(s) be included in the records, reporting sheets.

The brief sections that follow discuss the data value itself, recording and reporting the value in the proper way, means of quality control of data handling.

7.1 The Analytical Result Value

7.1.1 Significant Figures

The term significant figure is used rather loosely to describe some judgment of the number of reportable digits in a result. Often the judgment is not soundly based and meaningful digits are lost or meaningless digits are accepted.

Proper use of significant figures given an indication of the reliability of the analytical method used. Reported values should contain only significant figures. A value is made up of significant figures when it contains all digits known to be true and one last digit in doubt. For example, if a value is reported as 18.8 mg/l, the "18" must be firm values while the "0.8" is somewhat uncertain and may be "7" or "9".

The number zero may or may not be a significant figure:

- Final zeros after a decimal point are always significant figures. For example, 9.8 grams to the nearest mg is reported as 9.800 grams.
- Zeros before a decimal point with other preceding digits are significant. With no other preceding digit, a zero before the decimal point is not significant.
- If there are no digits preceding a decimal point, the zeros after the decimal point but preceding other digits are not significant. These zeros only indicate the position of the decimal point.
- Final zeros in a whole number may or may not be significant. In a conductivity measurement of 1000 µS/cm, there is no implication that the conductivity is 1000 $\pm$ 1 µS/cm. Rather, the zeros only indicate the magnitude of the number.

Significant figures reflect the limits of the particular method of analysis. It must be decided beforehand whether the number of significant digits is sufficient for interpretation purposes. If not, there is little that can be done within the limits of normal

laboratory operations to improve these values. If more significant figures are needed, a further improvement in method or selection of another method will be required to produce an increase in significant figures.

Once the number of significant figures is established for a type of analysis, data resulting from such analyses are reduced according to set rules for rounding off.

7.1.2 Rounding-Off Numbers

Rounding off of numbers is a necessary operation in all analytical areas. It is automatically applied by the limits of measurement of every instrument and all glassware. However, it is often applied in chemical calculations incorrectly by blind rule or prematurely, and in these instances, can seriously affect the final results. Rounding off should normally be applied only as follows:

7.1.2.1 Rounding-Off Rules

If the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. As an example: 11.43 is rounded off to 11.4.

If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by 1. As an example: 11.46 is rounded off to 11.5.

When the figure following those to be retained is 5, and there are no figures other than zeros beyond the 5, the figure is dropped, and the last place figure retained is increased by 1 if it is an odd number, or it is kept unchanged if an even number. As an example: 11.35 is rounded off to 11.4, while 11.25 is rounded off to 11.2.

7.1.2.2 Rounding-Off Single Arithmetic Operations

Addition: When adding a series of numbers, the sum should be rounded oft to the same numbers of decimal places as the addend with the smallest number of places. However, the operation is completed with all decimal places intact and rounding off is done afterward. As an example:

11.1
11.12
11.13
33.35 The sum is rounded-off to 33.4.

Subtraction: When subtracting one number from another, rounding off should be completed before the subtraction operation, to avoid invalidation of the whole operation.

Multiplication: When two numbers of unequal digits are to be multiplied, all digits are carried through the operation, then the product is rounded off to the number of significant digits of the less accurate number.

Division: When two numbers of unequal digits are to be divided, the division is carried out on the two numbers using all digits. Then the quotient is rounded off to the number of digits of the less accurate of the divisor or dividend.

Powers and Roots: When a number contains n significant digits, its root can be relied on for **n** digits, but its power can rarely be relied on for **n** digits.

7.1.3 Glossary of Terms

To clarify the meanings of reports and evaluations of data, the following terms are defined.

7.1.3.1 Accuracy Data
Measurements which relate to the difference between the average test results and the true result when the latter is known or assumed. The following measures apply:

- Bias is defined as error in a method, which systematically distorts results. The term is used interchangeably with accuracy in that bias is a measure of inaccuracy.
- Relative error is the mean error of a series of test results as a percentage of the true result.

7.1.3.2 Average
In ordinary usage, the arithmetic mean. The arithmetic mean of a set on n values is the sum of the values divided by n.

7.1.3.3 Characteristic
A property that can serve to differentiate between items. The differentiation may be either quantitative (by variables), or qualitative (by attributes).

7.1.3.4 Error
The difference between an observed value and its true value.

7.1.3.5 Mean
The sum of a series of test results divided by the number in the series. Arithmetic mean is understood (X).

7.1.3.6 Precision
Degree of mutual agreement among individual measurements. Relative to a method of test, precision is the degree of mutual agreement among individual measurements made under prescribed, like conditions.

7.1.3.7 Precision Data
Measurements, which relate to the variation among the test results themselves, i.e., the scatter or dispersion of a series of test results, without assumption of any prior information. The following measures apply:

- Standard Deviation (σ). The square root of the variance.
- Standard Deviation, estimate of universe (s)
- Coefficient of Variance (V). The ratio of the standard deviation (s) of a set of numbers, n, to their average, X, expressed as a percentage:
- Range. The difference between the largest and smallest values in a set.

- 95% Confidence Limits. The interval within which one estimates a given population parameter to lie, 95% of the time.

7.1.3.8 Sample
A group of units, or portion of material, taken from a larger collection of units, or quantity of material, which serves to provide information that can be used as a basis for judging the quality of the larger quantity as a basis for action on the larger quantity or on the production process. Also used in the sense of a "sample of observations."

7.1.3.9 Series
A number of test results which possess common properties that identify them uniquely.

7.1.3.10 Unit
An object on which a measurement or observation may be made.

7.1.3.11 Variable
A term used to designate a method of testing, whereby units are measured to determine, and to record for each unit, the numerical magnitude of the characteristic under consideration. This involves reading a scale of some kind.

7.2 Report Forms

The analytical information reported should include the parameter, the details of the analysis such as burette readings, absorbance, wavelength, normalities of reagents, correction factors, blanks, and finally, the reported value.

To reduce errors in manipulation of numbers, a good general rule is to keep data transposition to an absolute minimum. If this were pursued, the ideal report form would include all preliminary information of the analysis, yet it would be possible to use the same form through to the final reporting of data into a computer or other storage device. However, the ideal report form is not usually in use. Rather, a variety of methods are used to record data.

7.2.1 Loose Sheets

Reporting of data onto loose or ring-binder forms is an older, but much used means of recording data. It does allow easy addition of new sheets, removal of older data, or collection of specific data segments. However, the easy facility for addition or removal also permits easy loss or misplacement of sheets, mix-ups as to date sequence, and questionable status in formal display, or for presentation as evidence.

7.2.2 Bound Books

An improvement in data recording is use of bound books, which force the sequence of data insertion. Modification beyond a simple lined book improves its effectiveness with little additional effort. Numbering of pages encourages use in sequence and aids also in

referencing data, through a table of contents, according to time, type of analysis, kind of sample, analyst, etc.

Validation can be easily accomplished by requiring the analyst to date and sign each analysis on the day completed. This validation can be strengthened further by providing space for the laboratory supervisor to sign off as to the date and acceptability of the analysis.

A further development of the bound notebook is the commercially available version designed for research-type work. These note books are preprinted with book and page numbers and spaces for title of project, project number, analyst signature, witness signature and dates. Each report sheet has its detachable duplicate sheet which allows for up-to-date review by management without disruption of the book in the laboratory. The cost is about four times that of ordinary notebooks.

Use of bound notebooks is essentially limited to research and development work where an analysis is part of a relatively long project, and where the recording in the notebook is the prime disposition of the data until a status or final report is written.

7.2.3 Pre-Printed Report Forms

Most field laboratories or other installations doing repetitive analyses for many parameters day in and day out, develop their own system of recording and tabulating laboratory data. This may include bound notebooks, but a vehicle for forwarding data is also required. In many instances, laboratory units tailor a form to fit a specific group of analyses, or to report a single type of analysis for series of samples, with as much information as possible pre-printed to simplify use of the form. With loose-sheet multicopy forms information can be forwarded daily, weekly, or on whatever schedule is necessary, while allowing retention of all data in the laboratory. Still, the most common record is an internal bench sheet, or bound book, for recording of all data in rough form. The bench sheet or book never leaves the laboratory but serves as the source of information for all subsequent report forms.

In most instances the supervisor and analyst wish to look at the data from a sample point in relation to other sample points on the river or lake. This review of data by the supervisor, prior to release, is a very important part of the laboratory's quality control program; however, it is not easily accomplished with bench sheets. For this purpose, a summary sheet can be prepared which compares a related group of analyses from a number of stations. An example is shown in Figure 7-2. Since the form contains all of the information necessary for reporting data it is used also to complete the data forms forwarded to the storage and retrieval system.

The forms used to report data to data storage systems require a clear identification of the sample point, the parameter code, the type of analysis used, and the reporting terminology. Failure to provide the correct information can result in rejection of the data, or insertion in an incorrect parameter. As a group of analyses is completed on one or more samples, the values are reported in floating decimal form, along with true code numbers, for identifying the parameter and the sampling point (station).

7.2.4 Digital Read-out

Instrumental analyses, including automated, atomic absorption spectrophotometer, pH meter, etc., now can provide direct digital readout of concentration, which can be recorded directly onto report sheets without further calculation. Computers will construct best fit curves, integrate curves, and/or perform a pre-set series of calculations required to obtain the final reported value for recording by the analyst.

8 SKILLS

Analytical operations in the laboratory can be graded according to the degree of complexity. Some analyses require no sample treatment, with the measurement performed in minutes on a simple instrument. Other determinations require extensive sample preparation prior to complex instrumental examination. Consequently, work assignments in the laboratory should be clearly defined. Each analyst should be completely trained and fully understand all the assignments of his job before being given new responsibilities. In this regard, all analysts, sub-professional or professional, should be thoroughly instructed in basic laboratory operations, according to the degree of professional maturity. Some of the basic operations that should be reviewed periodically with laboratory personnel follow:

- Sample Logging. Emphasize the routine procedure for recording of samples entering the laboratory, and assign primary responsibility. Establish what information is required, and how sample is routed to analyst. Discuss stability of samples, and how they should be stored prior to analysis.

- Sample Handling. The analyst should understand thoroughly when the sample is to be settled, agitated, poured, pipetted, etc., before removal from the container.

- Measuring. The analysts, especially new employees and sub-professionals, should be instructed in the use of volumetric glassware. The correct use of pipettes and graduates should be emphasized as discussed earlier.

- Weighing. Because almost every measuring operation in the analytical laboratory is ultimately related to a weighing operation, the proper use of the analytical balance should be strongly emphasized. Maintenance of the balance, including periodic standardization, should be reiterated to all personnel.

- Glassware. All glassware should be washed and rinsed following the requirements of the analysis to be performed. Not only must the personnel assigned to this task be instructed, but all lab personnel should know the routine for washing glassware, and also special requirements for particular uses. In addition, the precision tools of the laboratory such as pipets, burets, graduates, Nessler tubes, etc., should be inspected before use for cleanliness, broken delivery tips, and clarity of marking. Defective glassware should be discarded or segregated.

In summary, quality control begins with basic laboratory techniques. Individual operator error and laboratory error can be minimized if approved techniques are consistently practiced. To insure the continued use of good technique, laboratory supervisors should periodically review the basic techniques with each analyst and point out, when necessary, areas of needed improvement.

Continuing improvement of technical competence for all laboratory personnel is, of course, the final responsibility of the laboratory supervisor. In a well-organized

laboratory, however, a big brother attitude of higher ranking to lower grade personnel should be encouraged; each person should be eager to share experience, tricks-of-the-trade, special skills, and special knowledge with subordinates. Obviously, improved efficiency and improved data quality will result.

8.1 Skills

The cost of data production in the analytical laboratory is based largely upon two factors-the pay scale of the analyst, and the number of data units produced per unit of time. However, estimates of the number of measurements that can be made per unit of time are difficult, because of the variety of factors involved. If the analyse is pushed to produce data at a rate beyond his capabilities, unreliable results may be produced. On the other hand, the analyst should be under some compulsion to produce a minimum number of measurements per unit of time, lest the cost of data production become prohibitive. In the following table, estimates are given for the number of determinations that an analyst should be expected to perform on a routine basis. The degree of skill required for reliable performance is also indicated. The arbitrary rating numbers for the degree of skill required are footnoted in the tables, but are explained more fully below:

- Rating 1-indicates an operation that can be performed by a semi-skilled sub-professional with limited background;
- Rating 2-operation requires an experienced aide (sub-professional) with background in general laboratory technique and some knowledge of chemistry, or a professional with modest training and experience;
- Rating 3-indicates a complex procedure requiring a good background in analytical techniques;
- Rating 4-a highly involved procedure requiring experience on complex instruments; determination requires specialization by analyst who interprets results.

A tacit assumption has been made that multiple analytical units are available for measurements requiring special equipment, as for cyanides, phenols, ammonia, nitrogen and COD. For some of the simple instrumental or simple volumetric measurements, it is assumed that other operations such as filtration, dilution or duplicate readings are required; in such cases the number of measurements performed per day may appear to be fewer than one would normally anticipate.

8.2 Training

For more experienced, higher grade personnel, formal training in special fields, possibly leading to specialization, should be almost mandatory. Such training can be fostered through local institutions and through the training courses.

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Annex 1.

ISO METHODS USED IN AQUATIC MONITORING

ISO 5667-1:1980 Sampling.
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ISO 5667-1:1991 Part 2: Guidance on sampling techniques

ISO 5667-3:1994 Part 3: Guidance on the preservation and handling of samples

ISO 5667-4:1987 Part 4: Guidance on sampling from lakes, natural and man-made

ISO 5667-6:1990 Part 6: Guidance on sampling of rivers and streams

ISO 5667-10:1992 Part 10: Guidance on sampling of waste waters

ISO 5667-12:1995 Part 12: Guidance on sampling of bottom sediments

ISO 5667-13:1997 Part 13: Guidance on sampling of sludges from sewage and water treatment works

ISO 5667-14:1998 Part 14: Guidance on quality assurance of environmental water sampling and handling

ISO 5667-15:1999 Part 15: Guidance on preservation and handling of sludge and sediment samples

ISO 5667-16:1998 Part 16: Guidance on biotesting of samples

ISO 5667-17:2000 Part 17: Guidance on sampling of suspended sediments

ISO 6341:1990 Water quality. Determination of the inhibition of the mobility of *Daphnia, magna*. Straus *(Claducera, Crustacea)*. Acute toxicity test.

ISO 10 712:1995 Water quality. Pseudomonas putida growth inhibition test. (Pseudomonas cell multiplication inhibition test)

ISO 7828:1985 Water quality. Methods of biological sampling. Guidance on handnet sampling of aquatic benthic macro-invertebrates

ISO 8265:1988 Water quality. Design and use of quantitative samplers for benthic macro-invertebrates on stony substrate in shallow freshwaters

ISO 8692:1989	Water quality. Freshwater algal growth inhibition test with Scenedesmus subspicatus and Selmastrum capricornutum
ISO 1189:1996	Water quality. Determination of phosphorus. Ammonium molybdate spectrometric methods.
ISO 1483:1997	Water quality. Determination of mercury.
ISO 1484:1997	Water analysis. Guidelines for teh determination of total organic carbon (TOC) and dissolved organic carbon (DOC).
ISO 7027:1990	Water quality. Determination of turbidity.
ISO 10260:1992	Water quality. Measurement of biochemical parameters. Spectrometric determination of chlorophyll-a concentration
ISO 10301:1997	Water quality. Determination of highly volatile halogenated hydrocarbons. Gas-chromatographic methods.
ISO 5813:1983	Water quality. Determination of dissolved oxygen. Iodometric methods.
ISO 5814:1990	Water quality. Determination of dissolved oxygen. Electrochemical probe method.
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ISO 5861:1994	Water quality. Determination of cadmium by atomic absorption spectrometry.
ISO 6058:1984	Water quality. Determination of calcium content. EDTA titrimetric method.
ISO 6060:1989	Water quality. Determination of chemical oxygen demand.
ISO 6332:1988	Water quality. Determination of iron. Spectrometric method using 1,10-phenanthroline.
ISO 6333:1986	Water quality. Determination of manganese. Formaldoxime spectrometric method.
ISO 6439:1990	Water quality. Determination of phenol index-4-Aminoantipyrine spectrometric method after distillation.
ISO 6468:1996	Water quality. Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes. Gas chromatographic method after liquid-liquid extraction.

ISO 6777:1984 Water quality. Determination of nitrite. Molecular absorption spectrometric method.

ISO 7150-1:1984 Water quality. Determination of ammonium.
Part 1: Manual spectrometric method.

ISO 7888:1985 Determination of electrical conductivity.

ISO 7890-3:1988 Water quality. Determination of nitrate.
Part 3: Spectrometric method using sulfosalicylic acid.

ISO 7980:1986 Water quality. Determination of calcium and magnesium. Atomic absorption spectrometric method.

ISO 9174:1990 Water quality. Determination of total chromium. Atomic absorption spectrometric method.

ISO 9297:1989 Water quality. Determination of chloride. Silver nitrate titration with chromate indicator (Mohr’s method)

ISO 9562:1989 Water quality. Determination of absorbable organic halogens (AOX).

ISO 9963-1:1994 Water quality. Determination of alkalinity.
Part 1: Determination of total and composite alkalinity.

ISO 9963-2:1994 Water quality. Determination of alkalinity.
Part 2: Determination of carbonate alkalinity.

ISO 9964-3:1993 Water quality. Determination of sodium and potassium.
Part 2: Determination of sodium and potassium by flame emission spectrometry.

ISO 10523:1994 Determination of pH.

ISO 11969:1996 Determination of arsenic. Atomic absorption spectrometric method (hydride technique).

Annex 2.

ANALYTICAL EQUIPMENT AND INSTRUMENTS

1. Analytical Balances

The analytical balance is an important piece of equipment in any analytical laboratory. It bears the same relationship to accuracy of measurements produced by a laboratory as the Greenwich standard clock has to international time-keeping. If the balance is not accurate all data related to weight-prepared standards will contain the same degree of error. The balance, therefore, should be the most protected cared-for instrument in the laboratory. Unfortunately, care of the balance is frequently overlooked.

There are many fine balances on the market designed to meet a variety of needs such as sensitivity, speed weighing, batch weighing, etc. Types of balances include general purpose, micro-, electro-, semi-analytical, analytical and other special purpose instruments. The analytical balance is one of the most important equipment in the production of reliable data.

Most analytical balances in use today in well-equipped laboratories are of the "single pan" variety. Single-pan capacities range from 80 grams to the 200-gram models with sensitivities from 0.01 to 0.1 mg. Features of single-pan balances include mechanical lifting and substitution of weights, digital readout of weights, and mechanical zeroing of the empty balance. The advantage of the single-pan balance over the old "two-pan" balance is in greatly increased weighing speed and improved weighing accuracy because of mechanical weight handling. With all the design improvements, however, the modern analytical balance is still a fragile instrument, subject to shock, temperature and humidity changes, mishandling and various other insults. Some of the precautions to be observed are as follows:

- Analytical balances should be mounted on a heavy shock-proof table, preferably one with adequate working surface; balance level should be checked frequently and adjusted when necessary.
- Balances should be located in separate room, protected from sudden drafts and humidify changes.
- Balance temperatures should be at room temperature; this is especially important if building heat is shut off or reduced during non-working hours.
- When not in use, the balance should be properly switched off, objects such as weighing dish removed from the pan and the slide door closed.
- Special precautions should be taken to avoid spillage of corrosive chemicals on the pan or inside the balance case; the interior of the balance housing should be kept clean.
- Balances should be checked and calibrated periodically by a company service man or follow the relevant manufacturer's instructions as closely as possible.
- The balance should be operated at all times according to the manufacturer's instructions.

Standardized weights to be used in checking balance accuracy, which may be purchased from various suppliers.

Since all analytical balances of the 200-gram capacity have about the same specifications with reference to sensitivity, precision, convenience, and price, and since these specifications are suitable for normal weighing requirements in water (environmental) laboratories, it is safe to assume that there is no clear preference for a certain model, and selection is best made on the basis of service availability.

2. pH Meters and Ion-selective Electrodes

A basic pH meter consists of a voltage source, amplifier, and readout device, either scale or digital. Certain additional refinements produce varying performance characteristics between models. Some models incorporate expanded scales for increased readability, operating stability and extreme accuracy. All instruments of recent design also include temperature adjustment and slope adjustment to correct for asymmetric potential of glass electrodes. Other features are scales that facilitate use of selective ion electrodes, recorder output, and interfacing with complex data handling systems.

In routine analytical work, the glass electrode is used as the indicator and the calomel electrode as the reference. Glass electrodes have a very fast response time in highly buffered solutions. However, accurate readings are obtained slowly in poorly buffered samples, and particularly when changing from buffered to un-buffered samples. Electrodes, both glass and calomel, should be well rinsed with distilled water after each reading, and should be rinsed or dipped several times into the next test sample before the final reading is taken. Weakly buffered samples should be stirred during measurement. Glass electrodes should not be allowed to become dry. When not in use they should be immersed in distilled water.

The first step in standardization of the instrument is done by immersing the glass and calomel electrodes into a buffer of known pH, setting the meter scale or needle to the pH of the buffer and adjusting the proper controls. The temperature compensating dial should be set at the sample temperature. The pH of the standard buffer should be within about two pH units of the sample. For best accuracy, the instrument should be calibrated against two buffers that bracket the pH of the samples.

The presence of a faulty electrode is indicated by failure to obtain a reasonably correct value for the pH of the second reference buffer solution after the meter has been standardized with the first. A cracked glass electrode will often yield pH readings that are essentially the same for both standards. The response of electrodes may also be impaired by failure to maintain the KCl level in the calomel electrode, or by certain specific materials such as oily substances and precipitates that may coat the surfaces. A faulty condition can be recognized from the check with the two buffer solutions. If either of these conditions should occur the electrode can probably be restored to normal by an appropriate cleaning procedure.

Because of the asymmetric potential of the glass electrode most pH meters are built with a "slope adjustment" which enables the analyst to correct for slight electrode errors that

occur when standardization is performed at two different pH levels. Details of slope adjustment and slope check may vary with different models of instruments. The slope adjustment must be made whenever electrodes are changed, subjected to vigorous cleaning, or refilled with fresh electrolyte.

Most pH meters are designed with a switching circuit so that the conventional 0-14 scale may be used to read a single pH unit. The "expanded-scale" feature allows for more accurate reading of the pH value and may be of value when the instrument is used for potentiometric titrations.

Solid state circuitry has led compact instruments suitable for field-work. Field-type instruments are generally battery-powered, and require more maintenance and more frequent standardization than laboratory instruments.

Standard buffer solutions, covering a range of pH, may be purchased from several chemical suppliers and are satisfactory for routine use. Table 5. gives a list of buffers (easily made in the laboratory) and the resulting pH at different temperatures. The effect of temperature on pH may be obtained by observing temperature as pH of various butters shown in the table. A rough rule is that: temperature compensation is about 0.05 pH units per 5 degree increase in temperature.

Table 5. pH values of buffers, in the range of 0 – 30 °C

Temp. °C	O.O5M Potassium Tetroxalate	Potassium Acid Tartarate (Saturated at 25°C)	O.O5 M Potassium Acid Phthalate	0.025 M Potassium Dihydrogen Phosphate+ 0.025 M Sodium Dihydrogen Phosphate	0.01 M Sodium Tetraborate
0	1.67	-	4.00	6.98	9.46
10	1.67	-	4.00	6.92	9.33
15	1 67	-	4.00	6.90	9.27
20	1.68	-	4.01	6.88	9.22
25	1.68	3.56	4.01	6.86	9.18
30	1.69	3.55	4.01	6.85	9.14

Typical performance data of a conventional scale pH meter is shown in Table 6.

Table 6. Performance characteristics of a typical pH meter.

	Normal Scale	Expanded Scale
Range	0 to 14 pH	1 pH
	±1400 mv	±100 mv
Smallest scale division	0.1 pH	0.005 pH
	10 mv	0.5 mv
Accuracy	±0.05 pH	±0.002 pH
	±5 mv	2% of reading
Reproducibility	±0.02 pH	±0.002 pH
	±2 mv	±0.2 mv
Temperature compensation	0 to I00°C (manual or automatic)	
Input impedance	$>10^{14}$	$>10^{13}$

2.1. Ion-selective Electrodes

In recent years a variety of ion-selective electrodes have been commercially available, and show great promise as fast and efficient tools for in situ monitoring and for laboratory analysis of all types of samples. A list of ions susceptible to analysis is indicative of the interest and progress being made in this field. Electrodes, or "probes" as they are popularly called, are available for measurement of monovalent cations, fluoride, sulphide, sulphate, nitrate, perchlorate, and a number of others. Dissolved oxygen probes should also be included in this list, although they are not technically ion-selective probes.

Ion-selective probes generally measure what they claim to measure, specific ion activity. They do not measure concentrations of un-ionised materials. For example, the probe designed to measure divalent cations promises to measure total hardness as a function of calcium and magnesium. However, since the probe does not respond to un-ionised calcium and magnesium, it does not accurately measure total hardness. As a consequence of this deficiency, much investigation is being carried out to devise means of determining total concentration of the constituent sought.

Standardised methods outlined procedures for use of two probes, fluoride and dissolved oxygen (DO). The chloride probe is also used on the automatic monitoring devices and considered as an approved procedure, together with the ion-selective electrodes for cyanide, ammonium and sulphide ions.

Personnel in water pollution laboratories are encouraged to investigate the use of ion-selective probes as a means of reducing analytical work and improving data quality. At the present time, however, only the fluoride, DO, and chloride probes are recommended for routine use in data collection.

A basic question relating to the use of ion-selective electrodes is the number of standards required to prepare a standard curve. It is generally agreed that the more standards used for the preparation of a colorimetric curve, the more reliable the data resulting from use of the curve. On the other hand, only one or two points are normally used in calibration of an instrument for measuring pH. conductivity or DO. In the conversion of a colorimetric procedure such as fluoride to a probe-type measurement, the tendency is to prepare a millivolt versus concentration curve using the usual six to 10 standards. Probe manufacturers insist that only one or two points are needed since the linearity of response has been established and only the slope of the line must be known. The alternatives are:

- Take readings in distilled water at 0 and at some concentration approximating concentration of sample: establish slope of line.
- Take readings in distilled water at 0 and two concentrations bracketing expected concentration of unknowns to establish curve or slope.
- Take readings at 0 and at decade concentrations as 1, 10, 100, etc., for standard curve.
- Take reading of sample, add known increment of measured constituent and read again; establish proportionality factor.

The method for the use of the fluoride electrode specifies use of multiple standards in the range between 0 to 2 mg/liter, because this system has supplied very precise data when compared to the colorimetric methods using the same set of standards. The system of incremental addition appears to have considerable merit since the electrode response is established in the presence of possible interference.

When an ion-selective electrode appears to be malfunctioning, the same check system may be used as for a faulty glass pH electrode. It is unlikely, however, that the electrode will be cracked, it will probably be dry, or insufficiently filled with the necessary solution. The probe assembly and instructions for refilling customarily accompany the item when shipped by the manufacturer and said instructions should be followed by the user.

Selective ion probes are available from several manufacturers.

3. Conductivity Meters

Solutions of electrolytes conduct an electric current by the migration of ions under the influence of an electric field. The current flowing between opposing electrodes immersed in the electrolyte will vary inversely with the resistance of the solution. The reciprocal of the resistance is called conductance and is expressed in reciprocal ohms or mhos. For natural water samples where the resistance is high, the usual reporting unit is in micromhos (μS/cm).

Practically all conductivity meters on the present market use direct read-out meter for indicating solution conductivity, and include a stepping switch for varying resistance in steps of 10X. The instruments are therefore capable of reading conductivity from about 0.1 μS/cm to about 250,000 μS/cm.

The sensing element for a conductivity measurement is the conductivity cell, which normally consists of two thin plates of platinized metal, rigidly supported with a very precise parallel spacing. For protection, the plates are mounted inside a glass tube, with openings in the side walls and submersible end for access of sample. Variations in designs have included use of hard rubber and plastics for protection of the cell plates. Glass may be preferable, in that the plates may be visually observed for cleanliness and possible damage.

In routine use, cells should be frequently examined to insure that (a) platinized coating of plates is intact, (b) plates are not coated with suspended matter, (c) plates are not bent, distorted, or misalign.

Temperature has a pronounced effect on the conductance of solutions, and must be corrected when results are reported. The specified temperature for reporting data used by most analytical groups is 25°C. Data correction may be accomplished by adjusting sample temperatures to 25 °C, or by use of mathematical or electronic adjustment. Adjustment of sample temperature is the preferred system, because of the empirical nature of the mathematical correction.

Instrumental troubles are seldom encountered with conductivity meters because of the design simplicity. When troubles occur they are usually in the cell, and for most accurate work the following procedures should be used:

- Standardize the cell and establish a cell factor by measuring the conductivity of a standard potassium chloride solution. Because the cell constants are subject to slow change, even under ideal conditions, and sometimes to more rapid change under adverse conditions, it is recommended that the cell constant be periodically established. Table 7. can be used for this operation,

- Rinse the cell by repeated immersion in distilled water,

- Again, immerse the cell in the sample several times before obtaining a reading.

Table 7. Electrical conductivity of potassium chloride reference solutions

Solution	Normality	Method of Preparation	Temp. (°C)	Conductivity (μS/cm)
A	0.1	7.4365 g KCl/l at 20 °C	0	7,138
			18	11,167
			25	12,856
B	0.01	0.7440 g KCl/l at 20 °C	0	773
			18	1,220
			25	1,408
C	0.001	Dilute 100 ml of B to 1 litre at 20 °C	25	147

For instruments reading in μS/cm, calculate the cell constant as follows:

$$L = \frac{K_1 + K_2}{1{,}000{,}000 \times K_x}$$

where

L = cell constant
K_1 = conductivity, in μS/cm, of the KCl solution at the temperature of measurement
K_2 = conductivity, in μS/cm, at the same temperature, of the distilled water used to prepare the reference solution
K_x = measured conductance, in μS/cm

4. Spectrophotometers

The spectrophotometer is an instrument for measuring an amount of light or radiant energy transmitted through a solution, as a function of wavelength. The different spectrophotometers uses different light radiations, which are summarised in Table 8. A spectrophotometer differs from a filter photometer, which uses continuously variable and more nearly monochromatic bands of light. Filter photometers are usually to enough

sensitive, and lack the versatility of spectrophotometers. They are used most profitably where a single method can be designed to fit the instrument.

Since a large portion of routine chemical analyses of water are performed colorimetrically, the spectrophotometer is usually a key instrument of the laboratory. The versatility of the instrument and the number of demands imposed upon it, have resulted in a large variety of designs and price ranges. As a matter of practicality, spectrophotometers are discussed separately as visible and ultraviolet, infrared, fluorescence and atomic absorption instruments.

The essential parts of a spectrophotometer are:

- A source of radiant energy, usually a tungsten filament bulb,
- The monochromator, a device for isolating narrow bands of light,
- Cells (cuvettes), for holding the coloured solution under investigation, and
- The photo-detector, a device to detect and measure the radiant energy passing through the sample.

Each of the essential features listed, especially the monochromator and the photo-detector system, vary in design principles from one instrument to another.

Table 8. Different radiations and approximate sizes of quanta

RADIATION	λ (cm) [typical values]	Wave-number (μm^{-1})	Size of quantum (electron volts)	Size of einstein (kilogram calories)	Absorption or emission of radiation involved
Gamma rays	10^{-10}	10^{6}	$1.2x10^{6}$	$2.9x10^{7}$	Nuclear reactions
X-rays	10^{-8}	10^{4}	$1.2x10^{4}$	$2.9x10^{5}$	Transitions of inner atomic electrons
Ultraviolet	10^{-5}	10	12	$2.9x10^{2}$	Transitions of outer atomic electrons
	$4x10^{-5}$	2.5	3.1	71	
Visible	$8x10^{-5}$	1.25	1.6	36	
Infrared	10^{-3}	10^{-1}	$1.2x10^{-1}$	2.9	Molecular vibrations
Far infrared	10^{-2}	10^{-2}	$1.2x10^{-2}$	$2.9x10^{-1}$	Molecular rotations
Radar **Long radio**	10	10^{-5}	$1.2x10^{-5}$	$2.9x10^{-4}$	Oscillation of mobile or free electrons

RADIATION	λ (cm) [typical values]	Wave-number (μm^{-1})	Size of quantum (electron volts)	Size of einstein (kilogram calories)	Absorption or emission of radiation involved
waves	10^5	10^{-9}	$1.2x10^{-9}$	$2.9x10^{-8}$	

4.1. Visible and Ultraviolet Spectrophotometers

Desirable features on a visible-range spectrophotometer are determined by the anticipated use of the instrument. Simple, limited measurement programme requires the analyses of only a few parameters at gross concentrations, which can be supported by an inexpensive, but reliable instrument. On the other hand, if a laboratory programme requires a wide variety of measurements on diverse samples at very low concentrations a more versatile instrument may be needed. One of the prime considerations would be adaptability to various cell sizes, at least from 1.0 to 5.0 cm. Many spectrophotometers now available are satisfactory for water quality analyses.

An ultraviolet spectrophotometer is similar in design to a visual range instrument, differences being in the light source and the optics. The light source is a hydrogen or deuterium discharge lamp, or xenon lamp, which emits radiation in the UV portion of the spectrum, generally from about 200 mμ to the low visible region. The optical system, the prism type, must be constructed of UV-transparent material, usually quartz. Sample cells must also be made of quartz or other UV-transparent material, if a grating system is used in an UV system, the grating may be specially cut (blazed) in the UV region for greater sensitivity. A number of spectrophotometers are available for use in both visible and ultraviolet wavelength range, called Vis-UV spectrophotometer.

4.2. Infrared Spectrophotometers

A number of instrumental changes are required in the construction of spectrophotometers for measurements in the infrared (IR) region. Modifications are needed, because optical materials such as glass and quartz, absorb radiant energy in the IR region and ordinary photocells do not respond.

Most IR spectrophotometers use front-surfaced mirrors to eliminate the necessity for radiant energy to pass through quartz, glass, or other lens materials. The mirrors are usually parabolic to facilitate gathering the diffuse IR energy. Instruments must be protected from high humidifies and water vapour to avoid deterioration of the optical system, and also to avoid extraneous absorption bands in the IR.

The energy or light source for an IR instrument may be a Nernst glower or a Globar. The detection unit may be a thermocouple, a bolometer, thermistor, or a photoconductor cell.

4.3. Fluorescence Spectrophotometers

The ultraviolet and visible regions of the spectrum are of most interest in fluorimetry and absorption in these regions causes the excitation of the outermost electrons of the molecule. The energy associated with radiation of this frequency is quite high, around 100 kilogram calories per einstein, and is sometimes sufficient to break down the absorbing molecules, as for instance with the fading of dyes by the action of sunlight. The absorption of light results in the formation of excited molecules which can in turn dissipate their energy by decomposition, reaction, or re-emission.

Since the emission of fluorescence always takes place from the lowest vibrational level of the first excited state, the shape of the emission spectrum is always the same, despite changing the wavelength of exciting light. A plot of emission against wavelength for any given excitation wavelength is known as the emission spectrum. If the wavelength of the exciting light is changed and the emission from the sample plotted against the wavelength of exciting light, the result is known as the excitation spectrum.

Since the amount of energy abstracted is always constant, Raman bands appear separated from the incident radiation by the same frequency difference, irrespective of the wavelength of the exciting light. If the Raman band of the solvent coincides with the fluorescence emission of the solute, separation can be achieved by changing the excitation wavelength to a lower value, hence the Raman band will also be lowered. Since the wavelength of fluorescence emission is independant of exciting wavelength the fluorescence will be separated from the Raman scatter. Raman scatter is only important at high sensitivity since the phenomenon is weak but must always be born in mind. The Raman emission of some solvents is quite complex and an emission spectrum of the solvent blank should always be run prior to the analysis. The wavelength of the Raman scatter in different solvents compared to selected excitation wavelengths is shown in Table 9.

Table 9. Positions of the most prominent Raman bands corresponding to various mercury lines

Solvent	Excitation wavelength (nm)				
	248	313	366	405	436
Water	271	350	418	469	511
Ethanol	267	344	410	459	500
Cyclohexane	267	344	409	458	499
Carbontetrachloride	-	320	376	418	450
Chloroform	-	346	411	461	502

All solvents containing hydrogen atoms linked to either carbon or oxygen show a Raman band shifted approximately 3000 cm^{-1} from the exciting radiation. If interference is observed, carbon tetrachloride or chloroform should be considered, since the main Raman bands of these solvents are much closer to the excitation wavelength.

Instruments

All fluorescence instruments contain three basic items, a source of light, a sample holder and a detector. In addition, to be of analytical use, the wavelength of incident radiation needs to be selectable and the detector signal capable of precise manipulation and presentation. In simple filter fluorimeters, the wavelengths of excited and emitted light are selected by filters, which allow measurements to be made at any pair of fixed wavelengths. Simple spectrofluorimeters have a means of analysing the spectral distribution of the light emitted from the sample, the fluorescence emission spectrum, which may be by means of either a continuously variable interference filter or a monochromator. In more sophisticated instruments monochromators are provided for both the selection of exciting light and the analysis of sample emission and such instruments are also capable of measuring the variation of emission intensity with exciting wavelength, the fluorescence excitation spectrum. In addition, synchronous scanning of both excitation and emission spectra might be usuful.

In principle the greatest sensitivity can be achieved by the use of filters, which allow the total range of wavelengths emitted by the sample to be collected, together with the highest intensity source possible. In practice, to realise the full potential of the technique, only a small band of emitted wavelengths are examined and the incident light intensity is not made excensive, to minimise the possible photodecomposition of the sample and to increase selectivity.

The majority of fluorescence assays are carried out in solution, the final measurment being made upon the sample contained in a cuvette. Cuvettes may be either circular, square or rectangular, and must be constructed of a material, e.g., silica, that will transmit both the incident and emitted light. Square cuvettes, or cells will be found most precise since the parameters of pathlength and parallelism are easier to maintain during manufacture.

The cuvette is placed normal to the incident beam, the resulting fluorescence is given off equally in all directions, and may be collected from either the front surface of the cell, at right angles to the incident beam, or in-line with the incident beam. Some instruments will provide the option of choosing which collecting method should be employed, a choice based upon the characteristics of the sample. A very dilute solution will produce fluorescence equally from any point along the path taken by the incident beam through the sample. Under these conditions the right angled collection method should be used since it has the benefit of minimising the effect of light scattering by the solution and cell. This is the usual measuring condition in analytical procedures. Although fluorescence takes place from every point along the light path, only a small fraction of this emission is actually collected by the instrument and transmitted to the detector.

The result is that much of the solution does not contribute to the fluorescence emission and the same intensity will be observed from a much smaller volume of solution contained in a microcell whose dimensions more closely match the optical considerations of the instrument.

As the absorbance of the solution increases the fluorescence emission becomes progressively distorted until a point is reached where little actually penetrates the main bulk of the solution and the fluorescence will be confined to the front surface of the cuvette. Front surface collection will still allow measurements to be made although the contribution due to light scattered from the cuvette wall will be large. Front surface collection will at least always show emission, possibly distorted, from a fluorescent sample whereas the fluorescence obtained from 90° collection falls rapidly as the absorbance of the solution increases. It is possible to dismiss a potential sample as non-fluorescent simply because the concentration is too high. Wherever possible the absorbance of a completely unknown solution should be measured before attempting a fluorescence check and the concentration adjusted to provide a solution of absorbance less than 0.1 A.

Other types of cuvette include flowcells, e.g., used in the monitoring of continuous flow systems, cells with thermostatted water jackets and micro or semi-micro cells. Fluorescence measurements can also be carried out on solid samples by means of the front surface collection technique.

Problems of High Blank Values

Cuvettes

One of the advantages of fluorescence procedures compared to equivalent absorption techniques is that routine measurements may be carried out in inexpensive test-tubes

rather than precision cuvettes without appreciable loss in precision. This benefit is derived from the geometrical layout of simple fluorimeters where only a small central area of the cuvette is actually viewed by the detector so that the overall dimensions of the cell are less important. However, this statement needs careful qualification since the use of laboratory grade test-tubes will result in deviation arising from other sources. Variations in cell wall width can give rise to errors by distorting the lens action of the round cell wall from one cell to another and the native fluorescence of the material used to manufacture the cell will often produce large blank values. Obviously the cell must be fabricated from a material which will transmit both the excitation and emission wavelengths of interest and if these are both in the visible region, savings can be made by the use of glass or even plastic sample containers. Only those cells recommended by the manufacturer of the instrument should be employed and every new batch should be carefully checked to make quite sure that their native fluorescence at the analytical wavelength chosen is minimal. Even the highest grades of silica and glass have some fluorescence although it should not contribute appreciably to routine measurements. Cells and other glassware used for fluorimetric analysis should be carefully cleaned, preferably by boiling in 50% nitric acid followed by thorough rinsing in distilled water.

Solvents and Reagents

The usable wavelength range of some common solvents is above their light absorption, and in most cases analytical reagent grade will be sufficiently pure. However, it is essential to examine the quality of solvents periodically since small traces of contaminants may be enough to produce high black values, particularly in some part of the féuorescence spectra. If the solvent blank is appreciable it can usually be reduced to a reasonable value by distillation or washing with acid, base or water. Water is the most common solvent and deionised-distilled water should always be employed. Solvents should not be stored in plastic containers since leaking of organic additives and plasticizers will produce high blank values. Fluorescence derived from contaminants should not be confused with the Raman scatter from the solvent itself. All other reagents used in the assay should be carefully controlled and high quality grades are to be recommended. Reagent blanks should always be carried through the analytical procedure and the actual value of the blank determined before the instrument is re-zeroed. High or changed blank values should immediately cast suspicion upon the solvents and reagents employed.

Inner-filter Effects

Fluorescence intensity will be reduced by the presence of any compound which is capable of absorbing a portion of either the excitation or emission energy. At high concentrations this can be caused by absorption due to the fluorophore itself. More commonly, particularly when working with tissue or urine extracts, it is the presence of relatively large quantities of other absorbing species that is troublesome. The purpose of extraction procedures is usually to eliminate such species so that the final measurement is made upon a solution essentially similar to the standard.

Application of Fluorescence Spectroscopy in Characterisation of Petroleum Pollutants.

A major element in several oil spill identification analytical methodology is fluorescence spectroscopy used in conjunction with gas-liquid chromatography, thin layer chromatography and infrared spectroscopy. Luminescence techniques are particularly attractive for the analysis of oil pills, or oil pollutants in water/sediment samples for the following reasons:

- Luminescence emanates mainly from the aromatic components of the hydrocarbon mixture. Not only are such components less subject to weathering than the aliphatic compounds, but they are generally more toxic than aliphatic compounds and hence of greater environmental importance.
- Fluorescence is generally more sensitive than conventional spectroscopic techniques and may therefore be applied to small quantities of sample.
- As a result of this sensitivity, direct application to aqueous samples - thus avoiding tedious purification procedures - and remote sensing, are feasible.

The application of luminescence phenomena to the identification of the source of an oil spill may be conveniently discussed in terms of (1) conventional fluorescence, (2) synchronous excitation fluorescence, and (3) total fluorescence techniques.

4.4. Atomic Absorption Spectrophotometers

There are a number of differences in the basic design and accessories for atomic absorption equipment that require consideration before purchase and during subsequent use. These choices concern the light source, the burners, optical systems, readout devices, and mode of conversion. Some of these choices are not readily obvious, and require that the purchaser or user be familiar with the types and numbers of samples to be analysed and the specific elements to be measured before a choice is made. For a programme analysing a wide variety of samples for a number of elements at varying concentrations, an instrument of maximum versatility would be required.

Lamp Mounts

A basic design feature of atomic absorption spectrometers is the convenience of the hollow cathode (HC) lamp changeover system. Some instruments provide for as many as six lamps in a rotating turret, all electronically stabilized and ready for use by simply rotating the lamp turret. Other instruments provide for use of only one lamp at a time in the lamp housing, and require manual removal and replacement whenever more than one element is to be measured. A quick changeover system is desirable, especially if a number of lamp changes are needed during a period of operation. Conversely, if lamp changes are infrequent, multi-lamp mounts do not represent a great convenience.

Fox optimal use of the instrument, certain precautions should be observed. After the proper lamp has been selected the hollow cathode current should be adjusted according to the manufacturer's recommendations and allowed to electronically stabilize (warm up) before use. This requires approximately 15 minutes. During this period, the monochromator may be positioned at the correct wavelength and the proper slit width selected. For those instruments employing a multi-lamp turret, a warm-up current is provided to those lamps not in use, thereby minimizing the warn-up period when the turret is rotated. In a single-lamp instrument, the instability exhibited during warm-up is minimized by the use of a double-beam optical system.

Single Element and Multi-Element Lamps

As an adjunct to single-lamp mounts, HC lamps using from two to as many as six elements in combination are available, thereby increasing the versatility of the atomic absorption spectrometer.

Multi-element lamps are considerably cheaper per element than single element lamps, but the savings may not realized if the lamps are not used strategically, because all the elements in the cathode deteriorate when the lamp is used, regardless of which element is measured. The deterioration phenomena results from the different volatilities of metals used in the cathode. One metal volatilises more rapidly than the others and re-deposits upon the cathode causing an increase in surface area of that metal, and decreasing the exposed area of the other cathode metals. Thus, with continual use, a drift in signal will be noted with at least one metal increasing and the other (or others) decreasing. The use of single-element lamps result in more precise and accurate data.

The individual line intensities of an element in a multi-element HC lamp will usually be less than that of a lamp containing a pure cathode of the same element. This is because each element must now share the discharge energy with all other elements present. However, this reduction should not affect the output by a factor of more than 1/2 to 1/6, depending on the combination and number of elements combined. The output can be even greater in multi-element lamps because alloying may permit a higher operating current than the cathode itself. All HC lamps have life expectancies, which are related to the volatility of the cathode metal. For this reason, the manufacturer's recommendations for amperage at which the lamp is operated should be closely followed.

A recent advance in HC lamp design, the high-intensity lamp, promises increased sensitivity for some elements. It is also predicted that the newly designed lamps will be used in atomic fluorescence techniques with significant gains in sensitivity.

Recent improvements in design and manufacture of hollow cathode lamps have resulted in lamps with more constant output and a longer life. Under normal conditions a HC lamp may be expected to operate satisfactorily for several years. Operating current and voltage will be indicated on the lamp and should not be exceeded during use. An increase in background noise and/or a loss of sensitivity are signs of lamp deterioration.

Burner Types

The most difficult and inefficient step in the AA process is converting the metal in the sample from an ion or a molecule to the neutral atomic state. It is the function of the atomizer and the burner to produce the desired neutral atomic condition of the elements. With minor modifications burners are the same as those used for flame photometry.

Basically there are two different types of burners. They are the total-consumption or surface-mix burner, and the laminar-flow or pre-mix burner. There are many variations of these two basic types, such as the Boling, the high-solids, the turbulent-flow, the tri-flame, nitrous-oxide burner and many others. As one might expect, there are many similarities among the various burners, the different names resulting from the different manufacturers. The element being determined and the type of sample solution dictate the type of burner to be used.

Generally, all types and makes of burners can be adjusted laterally, rotationally and vertically for selection of the most sensitive absorbing area of the flame for the specific element sought. The vertical adjustment is probably the most important since the position of greatest sensitivity varies from element to element.

Single- and Double-Beam Instruments

There is a great deal of existing uncertainty among instrument users about the relative merits of single-beam and double-beam instruments. Neither system is the final answer.

With a single-beam instrument the light beam from the source passes directly through the flame to the detector. In a double-beam system the light from the source is divided by a beam splitter into two paths. One path, the reference beam, goes directly to the detector. The second path, the sample beam, goes through the flame to the detector.

The chopper alternately reflects and passes each beam, creating two equal beams falling alternately upon the detector. If the beams are equal they cancel the alternate impulses reaching the detector and no signal is generated. If the beams are different, the resulting imbalance causes the detector to generate a signal, which is amplified and measured. Any difference between the reference and sample beam is measured as a direct function of absorbed light. The advantage of the double-beam design, therefore, is that any variations in the source are of reduced importance, and smaller dependence is placed upon the stability of the power supply. However, stabilization of the power supply can eliminate the apparent need for the split-beam system. Further, a beam splitter requires use of additional mirrors or optical accessories that cause some loss of radiant energy. Neither system, however, compensates for variation in flame intensity.

A single-beam system does not monitor source variations but offers certain other advantages. It allows use of low-intensity lamps, smaller slit settings and smaller gain. As a consequence, the single-beam instrument, properly designed, is capable of operating with lower noise, better signal-to-noise ratio and therefore better precision and improved sensitivity. Because the simplified optical system conserves radiant energy, especially in the shorter wavelengths, it facilitates operation in the low wavelength range. With this advantage, it should be possible to obtain better sensitivity for those elements with strong resonance lines below 350 nm, even those slightly below 300 nm.

Readout Devices

Early models of the AAS instrument offered only a meter, calibrated in percentage absorption. In the surge of competitive design, more sophisticated readout devices were built into or offered as accessories to various models. At the present time any desired readout method may be obtained with almost any instrument. Most of the instruments offer any combination of built-in digital scalers, calibrated in concentration, external digital printout in concentration, etc. Even inexpensive instruments are built with recorder interfacing.

Choice of a readout system is predicated largely upon laboratory needs and availability of budget. In general, any step toward complete automation is desirable but the degree of automation should be compatible with the laboratory programme.

Miscellaneous Accessories

Automatic sample changers are offered for almost all instruments on the market, and as has been previously stated, any automation feature is desirable. However, unless a laboratory programme performs a large number of repetitious measurements daily, an automatic sample changer would not be required.

4.5. Proper Use of Spectrophotometers

The manufacturer's instructions for proper use should be followed in all cases. Several safeguards against misuse of the instruments, however, are mandatory.

Instruments should be checked for wavelength alignment. If a particular coloured solution is to be used at a closely specified wavelength, considerable loss of sensitivity

can be encountered if the wavelength control is misaligned. In visual instruments, an excellent reference point is the maximum absorption for a dilute solution of potassium permanganate, which has a dual peak at 526 nm and 546 nm. On inexpensive grating instruments, which possess less resolution than the prism instruments, the permanganate peak appears at 525 to 550 nm as a single flat-topped spike.

For both UV and IR instruments, standard absorption curves for many organic materials have been published so that reference material for standard peaks is easily available. Standard films of styrene and other transparent plastics are available for IR wavelength checks.

Although most instruments contain built-in transformers for stabilization of the electronic circuits, an exterior, high capacity, constant-voltage transformer is recommended for general laboratory control.

Concerning the absorption cells, all cells should be kept clean, free of scratches, fingerprints, smudges and evaporated film residues. Matched cells should be checked to see that they are equivalent by placing portions of the same solution in both cells and taking several readings of the %T or absorbance values. If a cell is mismatched it should be discarded or reserved for rough work.

Generally speaking, trained technicians may operate any of the spectrophotometers successfully. However, interpretation of data from the sophisticated instruments becomes increasingly complex, and requires more training and specialization. IR and fluorescence interpretation requires special training, and because of the special techniques of sample preparation, instrument operation, and interpretation of absorption curves and spectra, mere compliance with the operations manual is not sufficient.

5. Total/Dissolved Organic Carbon Analyzer

Total organic carbon (TOC) as a measure of the carbon content of dissolved and undissolved organic matter present in the water is one of the principal parameters of water quality. In routine water analysis the organic pollution is generally described in terms of so called "non-specific" group parameters, such as biological oxygen demand (BOD), chemical oxygen demand (COD), total oxygen demand (TOD), total organic carbon (TOC) and UV absorption. Of these parameters, TOC is considered most relevant, since this parameter not only reflects the quantitative aspects of the organic pollution best, but accurate and rapid instrumental techniques are available for its measurement. TOC like the other "non-specific" parameters does not give information on the nature of the organic substance.

In addition to organic carbon the water sample may contain carbon dioxide or ions of carbonic acid. Prior to the TOC determination, it is essential that this inorganic carbon is removed by purging the acidified sample with a gas which is free from CO_2 and organic compounds. Alternatively, both total carbon (TC) and total inorganic carbon may be determined and the organic carbon content (TOC) may be calculated by subtracting the total inorganic carbon from the TC. This method is particularly suitable for samples in which the total inorganic carbon is less than the TOC.

Purgeable organic substances, such as benzene, toluene, cyclohexene, and chloroform may partly escape upon stripping. The TOC of these substances is therefore determined separately, or the differential method (TC - TIC = TOC) may be applied. By using the differential method, the value of the TOC needs to be higher than the TIC, or at least of similar size.

Cyanide, cyanate, and particles of elemental carbon (soot) when present in the sample, will be determined together with the organic carbon.

In the field of TOC determination the following definitions are used:

Total carbon (TC): The sum of organically bound and inorganically bound carbon present in water, including elemental carbon.

Total inorganic carbon (TIC): The sum of carbon present in water, consisting of elemental carbon, total carbon dioxide, carbon monoxide, cyanide, cyanate, and thiocyanate. TOC instruments mostly register as TIC only the CO_2 originating from hydrocarbonates and carbonates.

Total organic carbon (TOC): The sum of organically bound carbon present in water in dissolved form and/or associated with the suspended matter. Cyanate, elemental carbon and thiocyanate will also be measured.

Dissolved organic carbon (DOC): The sum of organically bound carbon present in water originating from compounds which will pass an 0.45 μm pore size membrane filter. Cyanate and thiocyanate are also measured.

Volatile organic carbon (VOC), (POC): Under the conditions of TOC measurement purgeable organic carbon.

Non volatile organic carbon (NVOC): Under the conditions of TOC measurement non-purgeable organic carbon.

The sample handling and processes considered during the TOC measurement are as follows:

- Inorganic carbon could be removed by acidification and purging or is determined separately.
- Oxidation of organic carbon in water to carbon dioxide by combustion, by the addition of an appropriate oxidant, by UV radiation or any other high-energy radiation.
- The application of the ultraviolet method with only oxygen as an oxidant is restricted to low polluted waters. Systems based on oxidation using UV energy are not suitable for the determination of microcellulose as an example for samples containing suspended matter (See Annex A, results from the interlaboratory test, sample a and 2 b).
- The carbon dioxide formed by oxidation is determined either directly or after reduction, for example, to methane (CH_4).

- The final determination of CO_2 is carried out by a number of different procedures, for example: Infrared spectrometry, titration (preferably in non-aqueous solution), thermal conductivity, conductometry, coulometry, CO_2-sensitive sensors and flame ionization detection. The later one is used after reduction of the CO_2 to methane.

A number of devices designed to measure the organic content of aqueous samples have appeared on the market within the last decades. The oldest, or first of these instruments, is the Beckman Carbonaceous Analyzer. The apparatus measures organic carbon as carbon, by oxidizing a very small sample at a temperature of 900°, in a stream of oxygen, converting all organically bound carbon to carbon dioxide, which is then measured by a Golay-type thermal detector. The instrument is able to detect about 20 mg of carbon. A modification of the original Beckman Carbonaceous Analyzer employs a dual-combustion-tube system operating at different temperatures to distinguish between total carbon and inorganic carbon. Organic carbon is found by difference.

Because there are several new instruments - even using different principles for digestion, combustion of the organic matter -, on the market, the determination of TOC concentrations of the samples in accordance with the instrument manufacturer's instructions. Some important considerations are asfollows:

- In the case of direct determination of the TOC, the total inorganic carbon (ensure that the pH is below 2) should be removed prior to analysis. Loss of volatile organic substances should be carefully minimised.
- The TOC concentration should be within the working rage of the calibration. This can be achieved by diluting the sample.
- Prior to each batch of TOC determinations (for example 10 determinations) carry out control experiments at the intervals recommended by the manufacturer, but at least daily.
- After acidification, blow a stream of pure inert gas free from CO_2 and organic impurities through the system (for approx. 5 min) in order to remove CO_2.

6. Adsorbable/Extractable Organic Halogens (AOX/EOX) Analyzer

Only a few natural substances contain halogens in their molecules, and chlorinated organic compounds are usually synthetically produced. Because of their favourable qualities, such as non-inflammability, great dissolving power and high reactivity, they have found widespread use in households and industry throughout the world. They are used in degreasing solvents, cooling liquids, insecticides, hydraulic and transformer fluids, dry cleaning and bleaching processes.

Unfortunately their environmental risk is also considerable. Most of them are resistant to biodegradation, they are lipophilic and concentrate in fatty tissue. As a consequence they remain in the biosphere for long periods, causing damage in many different ways. Although generalisation is not possible, it can be stated that, in addition to being acutely toxic to human beings, many organohalides are proven or suspected carcinogens. For example, discussions about dioxins and fluorochloro-hydrocarbons have raised much

public concern. Ever since the discovery that drinking water contains haloforms being formed by the reaction of the disinfectant chlorine with organic material, an intensive investigation of the sources and possible consequences has been in progress.

The extremely large number of organohalides that are of environmental concern has created a need for a method for their detection in effluents and drinking water. In order to avoid complicated and time-consuming analysis of single species within this category of compounds and for convenience, a general method for organohalogens was sought. The analysis of organohalogens in water itself is not possible, due to their low concentration and the considerably higher amount of inorganic chlorides. Thus a pretreatment for the isolation and concentration of the organic compounds and the separation of interfering inorganic compounds had to be developed.

In the early 1970s Kuhn and Sontheimer in Germany developed the AOX method for the analysis of organohalogens, consisting of adsorption on activated carbon, rinsing off the inorganic chlorides, pyrolysis of the organohalogens and microcoulometry. A variation of this method by Dressman led to the American EPA method 450.1. In Sweden, where the pulp industry produces large amounts of bleaching effluents, the TOCl method was developed, comprising adsorption on XAD resin and Schöniger combustion. The AOX method was standardised in Germany first (DIN 38409H14) and incorporated in official legislation. Having the highest recovery rates and being the most practicable, this method of determination has meanwhile come into worldwide use. In Sweden it has superseded the total organic chlorine (TOCl) method.

A criticism often raised is that the AOX method does not differentiate between hazardous and non-hazardous substances. Unfortunately there is no quick screening method available to identify hazardous compounds. Moreover, the multitude of organic materials in industrial effluents that can react in many different ways would render such methods ultimately unsatisfactory.

Principles

AOX is the determination of the amount of organic halogen that adsorbs on activated carbon. After combustion with oxygen at 900 oC, halide is detected by microcoulometric titration with silver.

Using the AOX method, organic chlorides, bromides and iodides can be quantitatively determined. The result is expressed in milligrams of chlorine per litre, regardless of the actual composition, because usually the chlorinated compounds constitute the overwhelming majority.

In the determination of the organohalides the organic micropollutants must be enriched and separated from interfering inorganic substances. The enriched organo-halides are converted to hydrogen halogens which are detected quantitatively. In the AOX method enrichment of the organic trace substances and displacement of the interfering inorganic substances are reached by means of adsorption onto activated carbon. After termination

of the enrichment procedure the loaded activated carbon is combusted in an oxygen atmosphere at a temperature of above 950 ^{o}C. The formed hydrogen halogens

The analysis can be divided into four different stages:

(a) Enrichment of the organic contaminants by adsorption on charcoal
(b) Removal of the inorganic halogens
(c) Formation of the hydrohalides by combustion in an oxygen stream
(d) Detection of halides.

German DIN method

Prior to adsorption, the water sample is acidified with nitric acid to enhance its affinity for charcoal. Then it is shaken with activated carbon; within one hour the organic compounds are adsorbed. A second method, also in common use, employs small columns filled with charcoal and connected in series, through which the water sample is pumped. After filtration with a membrane filter and rinsing with nitrate solution to remove the inorganic halogens, the filter with the carbon is transferred to a furnace. There it is pyrolysed in an oxygen flow at 1000 ^{o}C and the resulting hydrohalides are passed to a vessel containing sulphuric acid for drying. They then proceed to a microcoulometric titration cell where the halides react with silver ion, the concentration of which is maintained electrochemically, and are precipitated. The ion concentration drops and additional silver ion is generated. The charge required to generate that amount of silver ion is measured by an integration circuit and expressed in terms of micrograms of chlorine, which may be read from a digital meter on the instrument or calculated from a plotter diagram. The analysis of organic fluorides by this method is not possible because silver fluoride dissolves easily in the electrolyte.

This method was originally developed for drinking water and the detection limit is 10 μg. When analysing effluents some additional points have to be taken into account. First of all some samples may need to be homogenised using a magnetic stirrer, which is often the case with textile effluents. Also the DOC value (dissolved organic carbon) is very important. The DOC of an AOX sample must not exceed 10 mg/l, otherwise the charcoal would be overloaded and the adsorption would be incomplete. If the DOC values of samples exceed the 10 mg/l, the samples have to be diluted accordingly. The contents of inorganic chloride also have to be checked because more than 1 mg/l could interfere with the analysis. These conditions prove problematic on samples with high DOC values and low AOX values (< 0.5 mg/l).

If the sample is not to be analysed immediately after sampling, the liquor is acidified to pH 2 to prevent hydrolysis of the organic halides. To samples that may contain residual chlorine, sodium sulphite is added, to prevent further reaction and because free chlorine would lead to an incorrect AOX value. However, a reduction in AOX levels is observed by dechlorination with sulphite under neutral and basic conditions. This may be explained by hydrolysis or reaction of sulphite with the chlorinated compounds. Addition

of sulphite to acidic liquors, as recommended in the DIN standard, has negligible effects. Any form of sample pretreatment can influence the results, hence immediate analysis is recommendable.

This method detects hydrophilic and lipophilic or polar and non-polar compounds. The recovery varies with different substances, e.g., chlorophenols and other aromatic compounds range from 90 to 95%. Worst are the highly volatile compounds that adsorb very poorly and are better determined as **purgable organic halogen compounds** (POX). For POX analysis the sample is purged with oxygen in a vessel attached to the analyser and the purgable compounds are passed directly to the combustion unit. Afterwards the residual aqueous sample is used for AOX analysis.

A third possibility is the determination of **extractable organic halogen compounds** (EOX), which can also be used for sludges and soils. The lipophilic substances are extracted in hexane or pentane and injected directly into the furnace.

Considerations

There is still much discussion about the use of AOX as a meaningful environmental parameter. Environmental scientists urgently need a fast measurement of the degree of pollution in water, wastewater, soil, etc. Biological tests have proven that the compounds measured with AOX are really very harmful for all life on earth.

Among the increasing number of environmental tests to be specified, it is expected that AOX will be an important environmental parameter for many years to come.

Annex 3.

EQUIPMENT, INSTRUMENTS, TOOLS, CHEMICALS FOR WATER LABORATORIES

A. Conventional water chemistry laboratory

1.Sampling

Item	Size	Quantity
Bottles (PE or PP)	1000 ml	100
	250 ml	50
Bottles (brown glass)	1000 ml	100
Bottles (glass)	500 ml	100
Dropping bottles (glass)	50 ml	10

2. Sample preparation

Item	Size	Quantity
Membrane filters unit with cellulose nitrate/acetate membranes	0.45μm	250
Bottles for prepared samples	50 ml	50
	100 ml	100
	250 ml	50
	500 ml	10
	1000 ml	10
Graduated cylinders	10 ml	20
	25 ml	20
	50 ml	20
	100 ml	20
	250 ml	5
	500 ml	5
	1000 ml	5
Erlenmeyer flasks	50 ml	20
	100 ml	100
	250 ml	50
Stirrers		10
Dispensers	1000 ml	6
	500 ml	6
Automatic pipettes with tips	1-5 ml	2
	0.2-1 ml	2
Test-tubes	∅ 15 mm	100
Porcelain melting pots	∅ 50 mm	20

Item	Size	Quantity
Crucible tongs		2
Wash-bottle PE	1000ml	5
Pipettes	1 ml	5
(graduated, and with two signs)	2 ml	5
	5 ml	5
	10 ml	5
	25 ml	5
	50 ml	5
Funnels	50 mm	10
	150 mm	10
Burettes with stands	10 ml	10
	25 ml	2
Air-coolers		10
Soxlhett distilling apparatus	250 ml	10
Separating funnels	500 ml	5
	1000 ml	5
Exiccator	∅ 30 cm	1
Chemical spoons		5
Tweezers		2

3.Analysis

Instruments and accessories	Features	Quantity
Analytical balance	0.1 mg	1
Top-loading balance	0.1g	1
Magnetic stirrer		1
pH meter		1
Conductivity meter		1
Drying oven		1
Furnace		1
UV-VIS spectrophotometer with cuvettes (glass and quartz)		1
Sand-bath	6 plates	1
Heating plate		1
Refrigerator		2

4. Chemicals

pH paper
Acids
Standards
Distilled water
Reagents and measure solutions for methods

B. Trace inorganic water laboratory
(100-150 samples/month)

1. Sampling

Item	Size	Quantity (pcs.)
Bottles (PE or PP)	100, 250, 500 ml	100-100
Membrane filter unit with -cellulose nitrate/acetate membranes	0.45 µm	250
Dropping bottles (PE)	50 ml	10

2. Sample preparation

Item	Size	Quantity (pcs.)
Membrane filter unit with -cellulose nitrate/acetate membranes	0.45 µm	250
Bottles for prepared samples (PE or PP)	100, 250, 500 ml	100-100
Graduated cylinders PMP (TPX)	10, 25, 50, 100, 250, 500, 1000 ml	5-5
Beakers PMP (TPX)	10, 25, 50, 100, 250, 500, 1000 ml	10-10
Volumetric flasks PMP (TPX)	10, 25, 50, 100, 250, 500, 1000 ml	25-25 50-50 5-5
Erlenmeyer flasks PMP (TPX) and glass	50, 100, 250 ml	50-50
Stirrers PP		10
Dispensers	0.4-2 ml 2-10 ml 5-30 ml	1 1 1
Pipettes with tips	10 µl…10 ml	1-1
Funnels	50…150 mm	5-10
Wash-bottles PE	500 ml	5

Instruments and accessories	Features	Quantity (pcs.)
Analytical balance	0.1 mg	1
Top-loading balance	0.1 g	1
Hot plate & stirrer		1
Refrigerator for sample and reagent storage		2
Digestor a) Microwave system with -a rotor -medium and high pressure vessels (TFM) -water cooler -exhausting unit		 1 12-12 1 1
b) Stainless steel coated TFM bombs, -drying oven		25 1
c) Multi-unit extraction heater with -glass extraction apparatus	6-plate	 15

3. Analysis

Instruments and accessories	Features	Quantity (pcs.)
UV-VIS spectrophotometer with -cuvettes (glass and/or quartz)	 different	
Flame photometer		
AAS (flame, graphite furnace, hydride and cold vapour technique) with -hollow cathode lamps, -EDL power supply, -sample changer with vessels, -gas cylinders and regulators, -compressor, -graphite tubes		
ICP-OES with -sample charger with vessels, -gas cylinders and regulators		

4. Chemicals

pH papers
Acids (HCl, HNO_3, H_2O_2, H_2SO_4) Suprapur
Standards
High purity water
Reagents for AAS hydride and cold vapour technique
Matrix modifiers for AAS graphite furnace technique

C. Trace organic analytical water laboratory

1. Facilities

Item	Size	Quantity
Air conditioning		
Chemical hood		**5**

2. Sample preparation

Item	Size	Quantity
Dropping bottles		5
SPE cartridges	250 mg C_{18}	500
SPE cartridges	500 mg SiOH	500
ENVI C_{18} disk	47 mm	10 pk
Pipettes	1.2.5.10 mL	50
Beakers (glass)	25.50.75.150.500. 1000 mL	10.20.5.15.5.5
Volumetric Flasks (glass)	25.50.100.250. 500 mL	200
Petri dishes		50
Evaporating dishes		200
Funnels		10
Graduated cylinders	5.10.50.100.250. 1000 mL	15
Sampler bottles	150 mL 1000 mL 5000 mL	150 50 100

Instruments and accessories	Features	Quantity
Analytical balance	0.1 mg	1
Top-loading balance	0.1 gr	1
Semi-microanalytical balance		
Hot plate & stirrer		1
Drying oven		
Analytical mill		
Centrifuge + tubes		
Refrigerator for sample storage		3
Freezer for storage of standards and derivatization agents		3
pH meter + electrodes		1
Freeze-dryer		1
Instruments and accessories	**Features**	**Quantity**
Extractors a./ Microwave system b./ Ultrasonic bath c./ Soxhlett-glass apparatus with sand bath d./ Solid Phase Extraction equipment - vacuum manifold (12 or 24 port - ENVI disk apparatus	 6 places 	 1 1 3 2 10
Rotary vacuum pump		1
Water purification system		
Exiccator		2
Mortar and pestle		2
Sampling spoon		5
Spatulas		5
Tweezers		10
Pincers		1
Pliers		1
Wrench	6-31	15
Syringes + needles	5µL-250µL	50
Special tools for GC/MS instrument		

3. Analysis

Instruments and accessories	Features	Quantity
Gaschromatograph with auto-sampler		3
- gas cylinders and regulator		
- floow-meter		
- column	Apolar, polar	2,1
- septa		
- spli/splitless insert		5
- auto-sampler syringe		6
- ferrules		3 pk.
EC detector		
FI detector		
GC/MS instrument with spare parts		
- accessories same at GC		
HPLC with auto-sampler		
- gas cylinders and regulator		
- HPLC syringes		
- membrane filter		
- glass filter		
- syringe filter unit		3
- pre-filter		3 pk
- column		2
- guard-column		5
- eluent filtering and degassing assembly		2

4. Chemicals

pH papers
Acids (HCl, HNO_3, H_2O_2, H_2SO_4) Suprapure
Organic solvents (Suprapure for org. Trace analysis)
Standards
Deuterated standards for GC/MS
High purity water
Derivatization agents