الشركة القابضة
لمياه الشرب والصرف الصحى

برنامج المسار الوظيفي للعاملين بقطاع مياه الشرب والصرف الصحي

دليل المتدرب

البرنامج التدريبي كيميائي مياه

Atomic Absorption Spectroscopy - الدرجة الثالثة

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Atomic Absorption Spectroscopy

1. Theoretical Concepts and Definition.

The Atom and Atomic Spectroscopy.

The science of atomic spectroscopy has yielded three techniques for analytical use: atomic emission, atomic absorption, and atomic fluorescence. In order to understand the relationship of these techniques to each other, it is necessary to have an understanding of the atom itself and of the atomic process involved in each technique.

The atom is made up of a nucleus surrounded by electrons. Every element has a specific number of electrons which are associated with the atomic nucleus in an orbital structure which is unique to each element. The electrons occupy orbital positions in an orderly and predictable way.

The lowest energy, most stable electronic configuration of an atom, known as the ‘‘ground state’’, is the normal orbital configuration for an atom. If energy of the right magnitude is applied to an atom, the energy will be absorbed by the atom, and an outer electron will be promoted to a less stable configuration or ‘‘excited state’’. As this state is unstable, the atom will immediately and spontaneously return to its ground state configuration. The electron will return to its initial, stable orbital position, and radiant energy equivalent to the amount of energy initially absorbed in the excitation process will be emitted.

The process is illustrated in Figure (1-1). Note that in Step 1 of the process, the excitation is forced by supplying energy. The decay process in Step 2, involving the emission of light, occurs spontaneously.

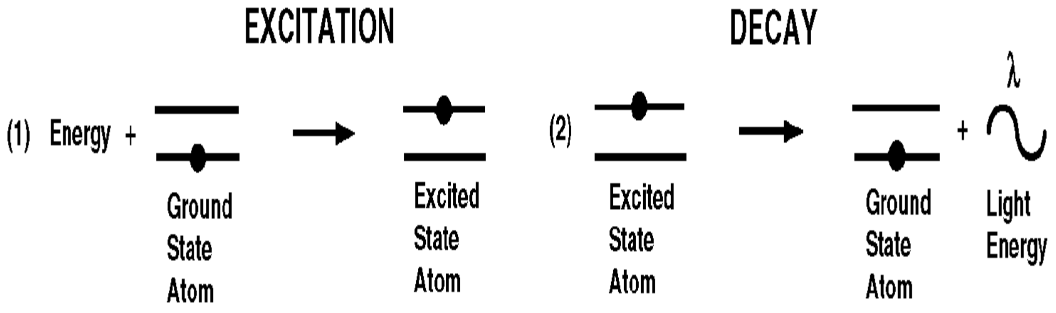

Figure (1-1). Excitation and decay processes

The wavelength of the emitted radiant energy is directly related to the electronic transition which has occurred. Since every element has a unique electronic structure, the wavelength of light emitted is a unique property of each individual element. As the orbital configuration of a large atom may be complex, there are many electronic transitions which can occur, each transition resulting in the emission of a characteristic wavelength of light, as illustrated in Figure (1-2).

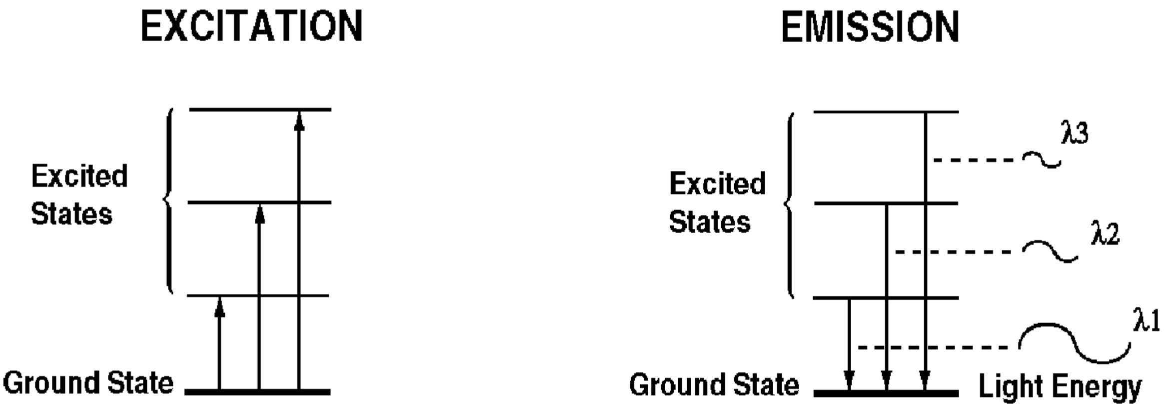

Figure (1-2). Energy transition states.

The process of excitation and decay to the ground state is involved in all three fields of atomic spectroscopy. Either the energy absorbed in the excitation process or the energy emitted in the decay process is measured and used for analytical purposes.

In atomic emission

A sample is subjected to a high energy, thermal environment in order to produce excited state atoms, capable of emitting light. The energy source can be an electrical arc, a flame, or more recently, plasma. The emission spectrum of an element exposed to such an energy source consists of a collection of the allowable emission wavelengths, commonly called emission lines, because of the discrete nature of the emitted wavelengths. This emission spectrum can be used as a unique characteristic for qualitative identification of the element.

Emission techniques

Also be used to determine how much of an element is present in a sample. For a ‘‘quantitative’’ analysis, the intensity of light emitted at the wavelength of the element to be determined is measured. The emission intensity at this wavelength will be greater as the number of atoms of the analyte element increases. The technique of flame photometry is an application of atomic emission for quantitative analysis.

If light of just the right wavelength impinges on a free, ground state atom, the atom may absorb the light as it enters an excited state in a process **known as atomic absorption**.

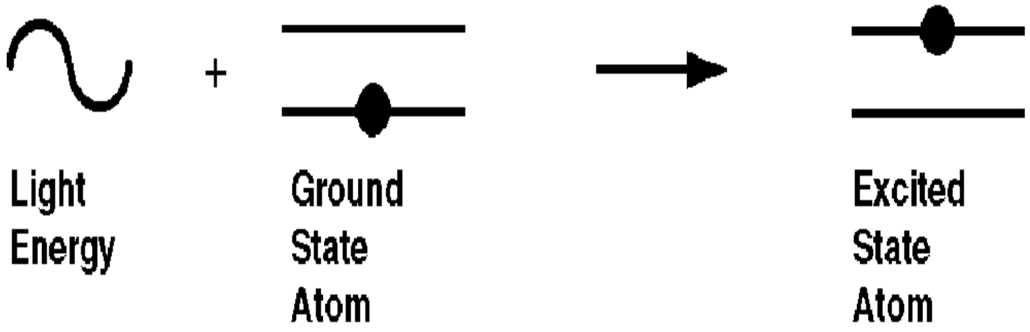

Figure (1-3). The atomic absorption process.

This process is illustrated in Figure (1-3). Note the similarity between this illustration and the one in Step 1 of Figure (1-1). The light which is the source of atom excitation in Figure (1-3) is simply a specific form of energy. The capability of an atom to absorb very specific wavelengths of light is utilized in atomic absorption spectrophotometry.

The atomic absorption process

The quantity of interest in atomic absorption measurements is the amount of light at the resonant wavelength which is absorbed as the light passes through a cloud of atoms. As the number of atoms in the light path increases, the amount of light absorbed increases in a predictable way. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte element present can be made. The use of special light sources and careful selection of wavelength allow the specific quantitative determination of individual elements in the presence of others.

A third field

In atomic spectroscopy is **atomic fluorescence**. This technique incorporates aspects of both atomic absorption and atomic emission. Like atomic absorption, ground state atoms created in a flame are excited by focusing a beam of light into the atomic vapor. Instead of looking at the amount of light absorbed in the process, however, the emission resulting from the decay of the atoms excited by the source light is measured. The intensity of this ‘‘fluorescence’’ increases with increasing atom concentration, providing the basis for quantitative determination.

The source lamp for atomic fluorescence is mounted at an angle to the rest of the optical system, so that the light detector sees only the fluorescence in the flame and not the light from the lamp itself. It is advantageous to maximize lamp intensity with atomic fluorescence since sensitivity is directly related to the number of excited atoms which is a function of the intensity of the exciting radiation. Figure (1-4) illustrates how the three techniques just described are implemented.

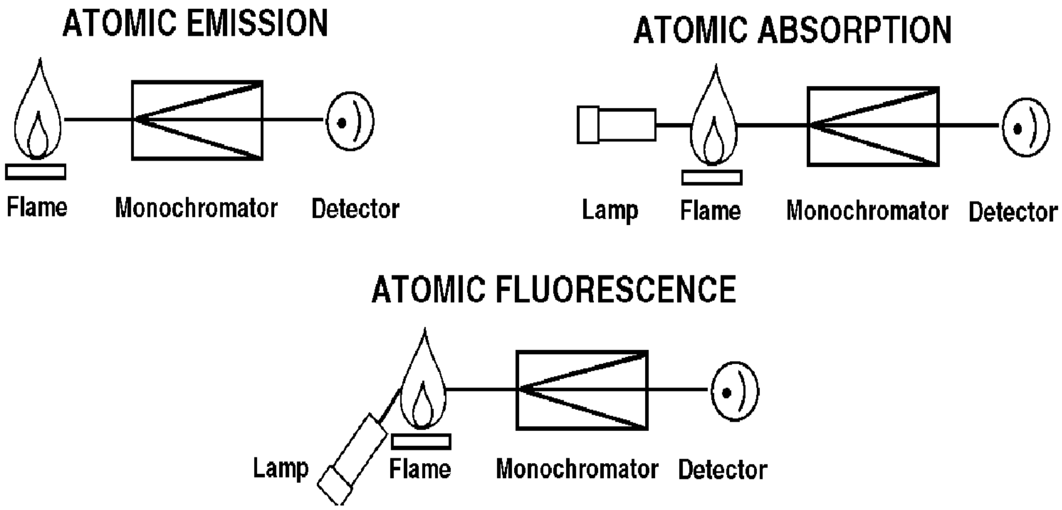

Figure (1-4). Atomic spectroscopy systems.

Quantitive Analysis By Atomic Absorption

The atomic absorption process is illustrated in Figure (1-5). Light at the resonance wavelength of initial intensity, Io, is focused on the flame cell containing ground state atoms. The initial light intensity is decreased by an amount determined by the atom concentration in the flame cell. The light is then directed onto the detector where the reduced intensity, (I), is measured. The amount of light absorbed is determined by comparing (I) to (I_o).

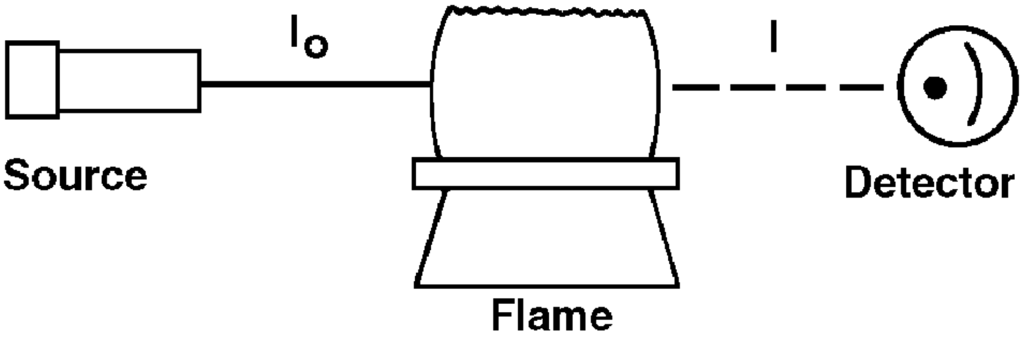

Figure (1-5). The atomic absorption process.

Several related terms are used to define the amount of light absorption which has taken place. The ‘‘transmittance’’ is defined as the ratio of the final intensity to the initial intensity.

$$T = I/I_o$$

Transmittance is an indication of the fraction of initial light which passes through the flame cell to fall on the detector. The ‘‘percent transmission’’ is simply the transmittance expressed in percentage terms.

$$\%T = 100 \times I/I_o$$

The ‘‘percent absorption’’ is the complement of percent transmission defining the percentage of the initial light intensity which is absorbed in the flame.

$$\%A = 100 - \%T$$

These terms are easy to visualize on a physical basis. The fourth term, ‘‘absorbance’’, is purely a mathematical quantity.

$$A = \log (I_o/I)$$

Absorbance is the most convenient term for characterizing light absorption in absorption spectrophotometry, as this quantity follows a linear relationship with concentration. Beer’s Law defines this relationship:

$$A = abc$$

Where:

‘‘A’’ is the absorbance.

‘‘a’’ is the absorption coefficient, a constant which is characteristic of the absorbing species at a specific wavelength.

‘‘b’’ is the length of the light path intercepted by the absorption species in the absorption cell.

‘‘c’’ is the concentration of the absorbing species. This equation simply states that the absorbance is directly proportional to the concentration of the absorbing species for a given set of instrumental conditions.

Characteristic Concentration and Detection Limits

Characteristic concentration and detection limit are terms which describe instrument performance characteristics for an analyte element. While both parameters depend on the absorbance observed for the element, each defines a different performance specification, and the information to be gained from each term is different.

Characteristic Concentration

The ‘‘characteristic concentration’’ (sometimes called ‘‘sensitivity’’) is a convention for defining the magnitude of the absorbance signal which will be produced by a given concentration of analyte. For flame atomic absorption, this term is expressed as the concentration of an element in milligrams per liter (mg/L) required producing a 1% absorption (0.0044 absorbance) signal.

$$\text{Char Conc. (mg/L)} = \frac{\text{conc of Std (mg/L)} \times 0.0044}{\text{measured absorbance}}$$

There are several practical reasons for wanting to know the value of the characteristic concentration for an element. Knowing the expected characteristic concentration allows an operator to determine if all instrumental conditions are optimized.

A known characteristic concentration value also allows one to predict the absorbance range which will be observed from a known concentration range or to determine the concentration range which would produce optimum absorbance levels.

Detection Limits

The smallest measurable concentration of an element will be determined by the magnitude of absorbance observed for the element (characteristic concentration) and the stability of the absorbance signal.

The detection limit is defined by the IUPAC as the concentration which will give an absorbance signal three times the magnitude of the baseline noise. The baseline noise may be statistically quantitated typically by making 10 or more replicate measurements of the baseline absorbance signal observed for an analytical blank, and determining the standard deviation of the measurements. The detection limit is then defined as the concentration which will produce an absorbance signal three times the standard deviation of the blank.

2 - Atomic Absorption Instrumentation

To understand the workings of the atomic absorption spectrometer, let us build one, piece by piece. Every absorption spectrometer must have components which fulfill the three basic requirements shown in Figure (2-1). There must be: (1) a light source; (2) a sample cell; and (3) a means of specific light measurement.

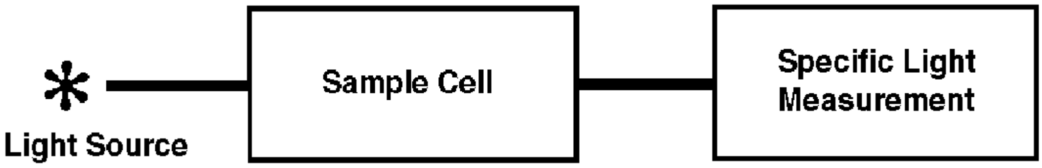

Figure (2-1). Requirements for spectrometer.

In atomic absorption, these functional areas are implemented by the components illustrated in Figure (2-2). A light source which emits the sharp atomic lines of the element to be determined is required. The most widely used source is the hollow cathode lamp. These lamps are designed to emit the atomic spectrum of a particular element, and specific lamps are selected for use depending on the element to be determined.

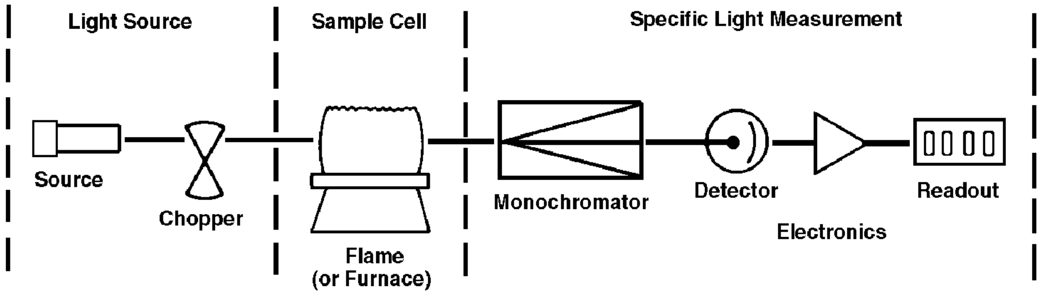

Figure (2-2). Basic AA spectrometer.

The Basic Components

1. AA Light Sources

An atom absorbs light at discrete wavelengths. In order to measure this narrow light absorption with maximum sensitivity, it is necessary to use a line source, which emits the specific wavelengths which can be absorbed by the atom. Narrow line sources not only provide high sensitivity, but also make atomic absorption a very specific analytical technique with little spectral interference.

The two most common line sources used in atomic absorption are the ‘‘hollow cathode lamp’’ and the ‘‘electrodeless discharge lamp.’’

A. The Hollow Cathode Lamp

The hollow cathode lamp is an excellent, bright line source for most of the elements determinable by atomic absorption. Figure (2-3) shows how a hollow cathode lamp is constructed.

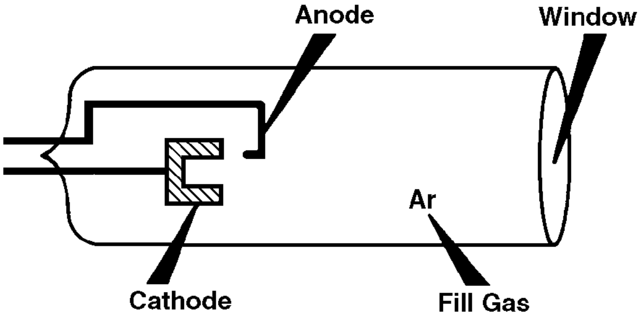

Figure (2-3). Hollow cathode lamp.

B. The Electrodeless Discharge Lamp

For most elements, the hollow cathode lamp is a completely satisfactory source for atomic absorption. In a few cases, however, the quality of the analysis is impaired by limitations of the hollow cathode lamp. The primary cases involve the more volatile elements where low intensity and short lamp life are a problem. The atomic absorption determination of these elements can often be dramatically improved with the use of brighter, more stable sources such as the ‘‘electrodeless discharge lamp’’. Figure (2-6) shows the design of the Perkin-Elmer System 2 electrodeless discharge lamp (EDL).

Electrodeless discharge lamps are typically much more intense and, in some cases, more sensitive than comparable hollow cathode lamps. Electrodeless discharge lamps are available for a wide variety of elements, including antimony, arsenic, bismuth, cadmium, cesium, germanium, lead, mercury, phosphorus, potassium, rubidium, selenium, tellurium, thallium, tin and zinc.

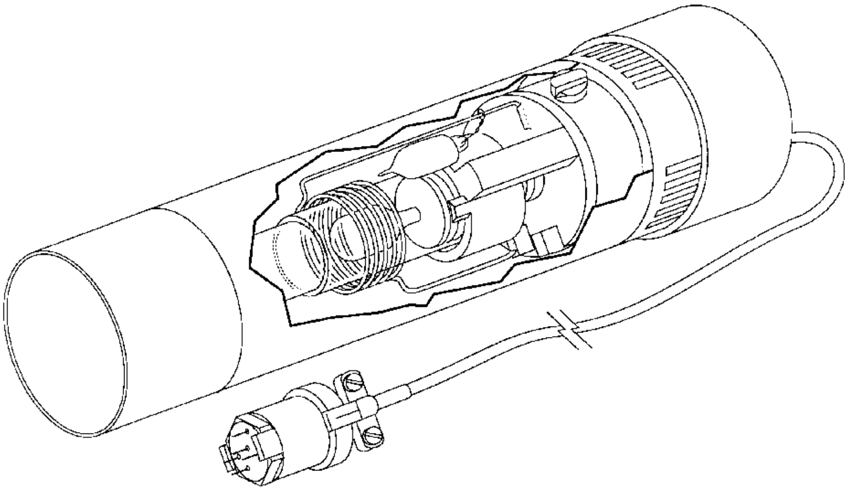

Figure (2-6). Electrodeless discharge lamp

2. Optical Considerations

Photometers

The portion of an atomic absorption spectrometer's optical system which conveys the light from the source to the monochromator is referred to as the photometer. Three types of photometers are typically used in atomic absorption instruments: single-beam, double-beam and what might be called compensated single-beam or pseudo double-beam.

Single-Beam Photometers

The instrument diagrammed in Figure (2-7) represents a fully functional ‘‘single beam’’ atomic absorption spectrometer. It is called ‘‘single-beam’’ because all measurements are based on the varying intensity of a single beam of light in a single optical path.

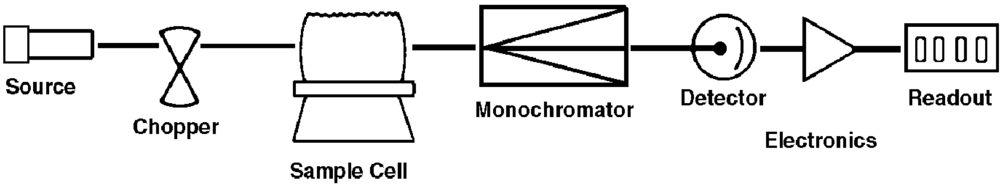

Figure (2-7). A single-beam AA spectrometer.

Double-Beam Photometers

An alternate photometer configuration, known as ‘‘double-beam’’ (Figure 2-8) uses additional optics to divide the light from the lamp into a ‘‘sample beam’’ (directed through the sample cell) and a ‘‘reference beam’’ (directed around the sample cell).

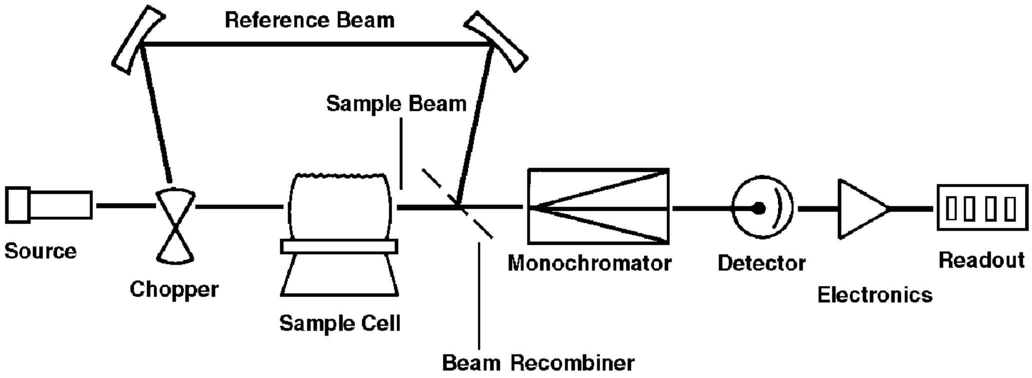

Figure (2-8). A double-beam AA spectrometer

Optics and the Monochromator System

Light from the source must be focused on the sample cell and directed to the monochromator, where the wavelengths of light are dispersed and the analytical line of interest is focused onto the detector. Some energy is lost at each optical surface along the way. Front-surfaced, highly reflective, mirrors can be used to control the focus of the source lamp and the field of view of the light detector precisely and with minimal light loss.

Particular care must be taken in the monochromator to avoid excessive light loss.

A typical monochromator is diagrammed in Figure (2-11).

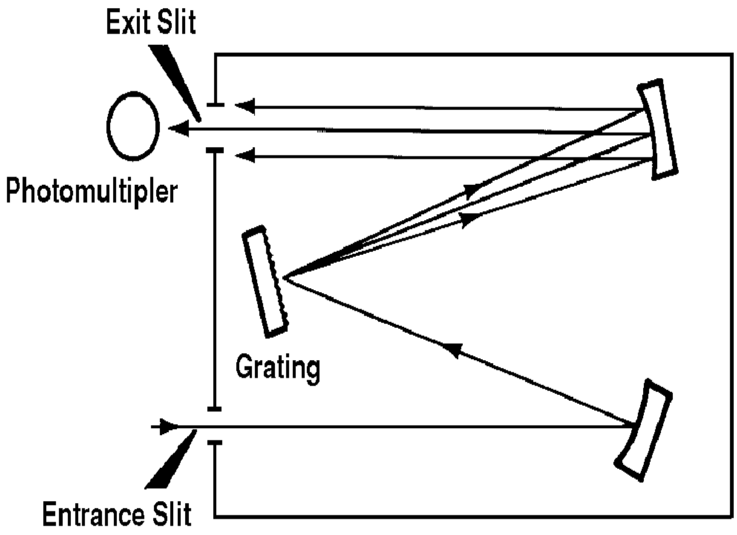

Figure (2-11). A monochromator.

Another factor affecting the optical efficiency of the monochromator is the blaze angle of the grating, whether it is mechanically ruled or holographically generated.

An illustration of a mechanically-ruled blaze angle appears in Figure (2-13).

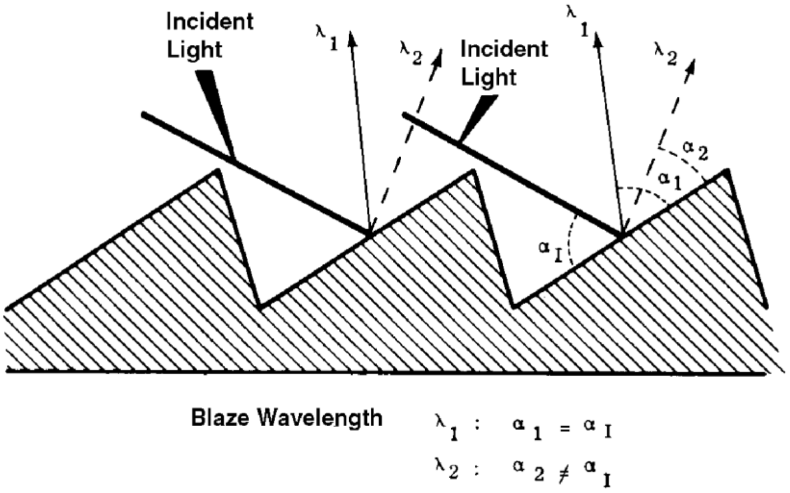

Figure (2-13). Grating blaze angle.

3. The Atomic Absorption Atomizer

Pre-Mix Burner System

Figure (2-14) shows an exploded view of an atomic absorption burner system. In this ‘‘premix’’ design, sample solution is aspirated through a nebulizer and sprayed as a fine aerosol into the mixing chamber. Here the sample aerosol is mixed with fuel and oxidant gases and carried to the burner head, where combustion and sample atomization occur.

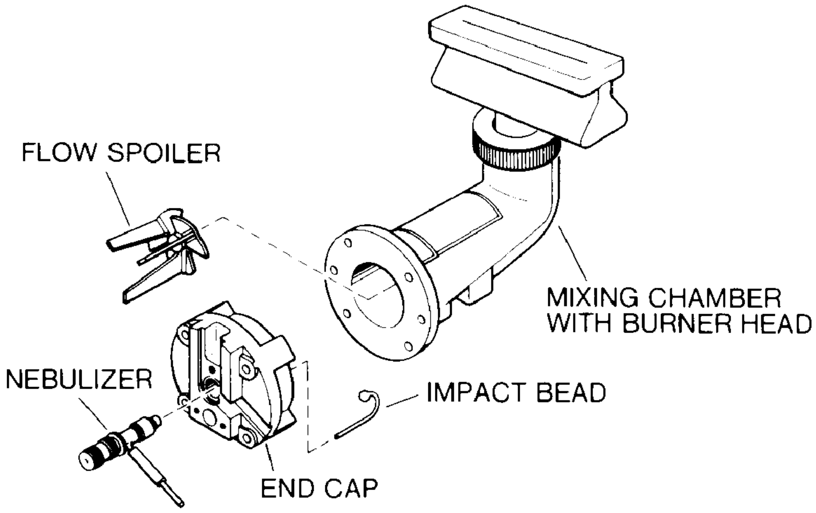

Figure (2-14). Premix burner system.

Only a portion of the sample solution introduced into the burner chamber by the nebulizer is used for analysis. The finest droplets of sample mist, or aerosol, are carried with the combustion gases to the burner head, where atomization takes place. The excess sample is removed from the premix chamber through a drain. The drain uses a liquid trap to prevent combustion gases from escaping through the drain line. The inside of the burner chamber is coated with a wettable inert plastic material to provide free drainage of excess sample and prevent burner chamber ‘‘memory.’’ A free draining burner chamber rapidly reaches equilibrium, usually requiring less than two seconds for the absorbance to respond fully sampling changes.

Impact Devices

The sample aerosol is composed of variously sized droplets as it is sprayed into the mixing chamber.

Impact devices are used to reduce droplet size further and to cause remaining larger droplets to be deflected from the gas stream and removed from the burner through the drain. Two types of impact device are used typically, impact beads and flow spoilers.

Impact bead systems are normally used to improve nebulization efficiency, the percentage of sample solution converted to smaller droplets. The impact bead is normally a spherical bead made of glass, silica or ceramic. Glass or quartz impact beads may be less corrosion resistant and may cause more contamination problems than more chemically inert ceramic beads.

Flow spoilers normally do not improve nebulization efficiency. The primary use of a flow spoiler is to remove the remaining large droplets from the sample aerosol. The flow spoilers used in atomic absorption burner systems normally are placed between the nebulizer and the burner head.

For routine atomic absorption analyses where maximum sensitivity is not required, use of an efficient flow spoiler alone will provide the required analytical stability and freedom from interference. A burner system optimized for maximum sensitivity and performance should include both a high nebulization efficiency ceramic impact bead and an efficient flow spoiler.

Nebulizers, Burner Heads and Mounting Systems

Several important factors enter into the nebulizer portion of the burner system. In order to provide efficient nebulization for all types of sample solution, the nebulizer should be adjustable, nebulizers constructed of a corrosion resistant material, such as an inert plastic, platinum alloys or tantalum should be used.

Burner heads typically are constructed of stainless steel or titanium. All-titanium heads are preferred as they provide extreme resistance to heat and corrosion

Different burner head geometries are required for various flame or sample conditions. A ten-centimeter single-slot burner head is recommended for air acetylene flames. A special five-centimeter burner head with a narrower slot is required when a nitrous oxide-acetylene flame is to be used. Burner heads also are available for special purposes, such as use with solutions that have exceptionally high dissolved solids contents.

Different AAS- technique

1- Flame technique
2- Non flame techniques
    a- Graphite furnace technique
    b- Hydride generation

1. Flame technique

Introduction

Flame-AAS is a single element technique with analyte determinations in the mg/1 region as routine for most elements

Principles

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

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

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

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

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

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

Interferences:

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

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

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

Ionization interference

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

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

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

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

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

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

Chemical interference

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

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

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

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

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

Physical interference:

a) If the physical properties as viscosity and surface tension vary considerably between samples and standards, the sample uptake rate or nebulization efficiency may be different and lead to erroneous results.

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

Background absorption and light scattering:

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

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

c) The background absorption can be accounted for by using background correction techniques such as continuous light source (D_2-lamp) or Smith-Hieftje.

Calibration standards:

- Calibration standards are prepared by single or multiple dilutions of the stock metal solution.
- Prepare a reagent blank and at least 3 calibration standards in graduated amount in the appropriate range of the linear part of the curve.

- The calibration standards must contain the same acid concentration as will result in the samples following processing.
- The calibration standard should be transferred to polyethylene bottles.

Instrumental procedure:

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

2- The position of observation and the fuel: oxidant ratio must be optimized.

3- Some general guidelines are outlined below

4- Light the hollow cathode lamp or electrode discharge lamp and D_2-lamp if such background correction is used.

5- Set the lamp current to the value specified by the manufacturer.

6- Position the monocromator at wavelength 213.9nm and choose slit with 0.7 and slit height “high”.

7- Carefully balance the intensity of the hollow cathode lamp and the D_2-lamp if such background correction is used.

8- Align the burner head to assure that the centre of the light beam passes over the burner slot.

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

10- Aspirate calibration blank and establish a zero point.

11- Aspirate standard solutions and construct a calibration curve.

12- Aspirate distilled water after each standard or sample.

Instrument performance:

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

The “characteristic concentration” is instrument dependent and is calculated as follows:

C_m = (S× 0.0044 AU) / measured absorbance

C: Characteristic concentration (mg L^{-1})

S: Concentration of measured standard (mg L^{-1})

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

Sequence of analysis:

- Aspirate calibration blank and establish a blank level
- Aspirate calibration blank and standard solutions and construct a calibration curve.
- Use at least 3 standard solutions in addition to the calibration blank to cover the linear range. Every point at the calibration curve should, if possible, be based on replicate analysis.
- Distilled water should be aspirated after each standard and sample.
- A quality control standard should be analysed to verify the calibration.
- A calibration blank should be analysed to check for memory effects.
- Aspirate unknown samples.
- Aspirate a quality control standard for every 10th sample to check for drift.
- Samples that are found to have concentration higher than the highest standard should be diluted and reanalyzed.

2. Non flame techniques:
A. Graphite furnace technique:

Introduction:

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

Principles:

- A graphite tube is located in the sample compartment of an AA spectrometer with the light from an external light source passing through it.
- A small volume of sample is placed inside the tube, which then is heated by applying a voltage across its ends.
- The analyte is dissociated from its chemical bonds and the fraction of analyte atoms in the ground state will absorb portions of light.
- The attenuation of the light beam is measured.
- As the analyte atoms are created and diffuse out of the tube, the absorption raises and falls in a peak-shaped signal.
- Beer-Lamberts law describes the relation between the measured attenuation and concentration of analyte.

GRAPHITE TUBES (FURNACES) TYPES

Pyrolytically coated tube:

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

Tube with platform: (L'vov's platform)

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

Things which effect to the service life of tube

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

Interferences:

1. Spectral interference:

A. Background absorption:

- The narrow bandwidth of hollow cathode lamps makes spectral overlap rare. That is, it is unlikely that an absorption line from one element will overlap with another.
- Molecular emission is much broader, so it is more likely that some molecular absorption band will overlap with an atomic line. This can result in artificially high absorption and an improperly high calculation for the concentration in the solution.
- Background absorption is non-specific attenuation of radiation at the analyte wavelength caused by matrix components.
- Enhanced matrix removal due to matrix modification may reduce background absorption.

- To compensate for background absorption, correction techniques such as continuous light source (D_2-lamp), Zeeman or Smith-Hieftje should be used.

Three methods are typically used to correct for this:

A. 1. Zeeman correction:

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

B. Smith-Hieftje correction:

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

C. Deuterium lamp correction:

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

2. Non-spectral interference (Matrix effect):

- Non-spectral interference arises when components of the sample matrix alter the vaporization behavior of the particles that contains the analyte.
- To compensate for this kind of interference, method of standard addition can be used.
- Enhanced matrix removal by matrix modification or the use of a L´vov platform may also lead to a reduction of non-spectral interferences.

Instrumentation

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

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

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

d) Pyrolytically coated graphite tubes.

Setting up a temperature program

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

A. Drying step:

i. A quick ramp (5 s) to 15 ^{o}C below the boiling point of the solvent. Then a slow ramp (25 sec) to reach a temperature just above the solvents boiling point.

ii. This provides a gentle evaporation without sputtering.

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

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

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

B. Pyrolysis step:

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

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

iii. In a pyrolysis step a typical ramp will vary between 20-50 ^{o}C/sec.

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

C. Atomization step:

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

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

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

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

D. Cleaning step:

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

xi. A purge gas flow of 250-300 ml min^{-1} is normally used.

Instrument performance:

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

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

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

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

$m_o = V_s \times C_s \times 0.0044$ AU / observed peak area

m_o: Characteristic mass (ng)

V_s: Standard volume injected (ml)

C_s : Standard concentration (ng ml^{-1})

Chemical modifiers:

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

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

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

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

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

Table 1. Proposed instrument parameters.

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

Sequence of analysis

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

b) If a significant signal is obtained, a cleaning step (2650 ^{o}C, 2-3 sec) should be run repetitively to remove the remains in the tube.

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

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

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

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

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

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

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

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

b- Hydride generation method:

This technique makes use of the property that the metalloid elements (i.e.: As, Se, Sb, Bi, Se, Te, Ge , Hg, and Pb) exhibit, i.e. the formation of covalent, gaseous hydrides which are not very stable at high temperatures..

The hydrides of arsenic, selenium, tellurium, antimony, bismuth and tin (and to lesser degree lead and germanium) are volatilized by the addition of reducing agent like sodium tetrahydroborate(III) to an acidified solution. Other systems have used titanium(III) chloride/magnesium powder and tin(II) chloride/potassium iodide/zinc powder as reducing agents.

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

Hydride Generation Analysis

- Hydride generation – elements which form gaseous hydrides: Sb, As, Bi, Se, Te, Sn – HGAAS.
- Acidified sample solution is reacted with $NaBH_4$ producing the analyte hydride, which is carried on a stream of argon carrier gas to the atomizer.
- The hydride decomposes in the atomizer to the elemental form and can be measured.
- A number of elements such as arsenic and selenium form volatile hydrides on reduction of their salts with suitable reducing agents such as sodium borohydride.
- Atomic absorption of the free atoms of the analyte element then occurs in the same way as with the flame or with an electrically heated cell.
- Mercury can be determined in the same way but in this case the inorganic mercury present in the samples is reduced to atomic mercury, which can then be swept into the absorption tube where the atomic absorption process occurs.
- This analysis the tube does not need to be heated as the free atoms are generated at room temperature.Hence the name Cold Vapor AAS.

The basic theory is that

1. The acidified sample solution is reacted with $NaBH_4$ producing the analyte hydride, which is carried on a stream of argon carrier gas to the atomizer.
2. The hydride decomposes in the atomizer to the elemental form and can be measured

Now for the science

1. Acidify sample.
2. Mix with reluctant.
3. Sodium borohydride $NaBH_4$.
4. Analyte reduced to gaseous hydride.
5. As^{3+} + BH_4^- + H^+ -> AsH_3 (gas) + BO_3 + H_2
6. Gaseous analyte hydride separated from liquid reagents.
7. Gas liquid separator device.
8. Gaseous analyte hydride carried into heated cell.
9. Inert (e.g. Ar, N_2) used to transport it.
10. Analyte atomized, and AA signal measured

2. Flow Injection Operation:

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

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

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

d) The signal is measured as a peak

3. Continuous Flow:

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

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

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

المراجع

- **تم الإعداد بمشاركة المشروع الألماني GIZ**
- **و مشاركة السادة :-**

➢ د/ سناء أحمد الإله	شركة مياه الشرب والصرف الصحى بالفيوم
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➢ د/ مى صادق	شركة مياه الشرب بالقاهرة الكبرى