USGS
science for a changing world

Techniques of Water-Resources Investigations
of the United States Geological Survey

Chapter A1

METHODS FOR DETERMINATION OF INORGANIC SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

By Marvin J. Fishman and Linda C. Friedman, Editors

First Edition 1970
Second Edition 1979
Third Edition 1989

Book 5
LABORATORY ANALYSIS

Laboratory Equipment and Techniques

Glassware and other containers

All glass apparatus and containers used in analytical work must be carefully selected to meet the requirements of their particular use. Although several types of special-purpose glasses are available, borosilicate thermal-resistant types, such as Pyrex or Kimax, are generally satisfactory for all ordinary laboratory purposes in water analysis. Borosilicate glass is especially suitable for storage of neutral or acid solutions, for volumetric glassware, and for conducting reactions. Because borosilicate glass is not entirely resistant to attack by strongly alkaline solutions, bottles of polyethylene or Teflon need to be used for storage of standard solutions of silica, boron, and alkali-metals hydroxides.

All volumetric glassware, such as burets, pipets, and volumetric flasks, must be of borosilicate glass and must contain or deliver volumes within the tolerances of the method. In addition if such glassware is frequently used to measure strongly alkaline solutions, it needs to be recalibrated at frequent intervals. Directions for such calibration and testing of volumetric glassware are given by the National Bureau of Standards (1959) and in standard texts of quantitative analysis.

Evaporations may be carried out in glass, porcelain, zirconium, or platinum dishes. Platinum is preferred if the weight of the residue needs to be determined accurately, because the weight of platinum vessels is relatively constant.

Although platinum is one of the most resistant metals, it is not completely inert and is subject to embrittlement. The following precautions are recommended: Never put solutions containing tin, mercury, or lead in a reducing environment in platinum; if the free metal should be formed it will alloy with the platinum, especially if heated. Do not heat mixtures of hydrochloric acid with oxidizing substances, such as nitrate or manganese dioxide; ferric chloride in hydrochloric acid attacks platinum appreciably. Place hot platinum vessels on a refractory material, never on a cold metal surface or on a dirty surface. Use only clean platinum-tipped tongs to handle hot platinum vessels. Coarse crystal growth and embrittlement may result from prolonged heating at high temperatures, heating under reducing conditions, and heating phosphates or sulfates in the presence of organic compounds. Embrittlement can be counteracted by rubbing the platinumware with moistened sea sand. Gentle rubbing with sea sand cold-works the metal and breaks down the coarse crystal structure. Detailed instructions for the care and use of platinumware are distributed by manufacturers of these vessels and are described in textbooks of quantitative analysis.

Chemicals and solutions

Purity

Unless otherwise indicated, all chemicals specified for use in analytical procedures shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Those chemicals not listed by this organization may be tested as indicated by Rosin (1955). Chemicals used for primary standards may be obtained from the National Bureau of Standards or from manufacturers marketing chemicals of comparable purity. Certified standard solutions may also be purchased.

Water used to dilute samples or to prepare chemical solutions shall first be demineralized by passage through mixed cation-anion exchange resins or by distillation. Its specific conductance at 25 °C must not exceed 1.0 μS/cm, and it shall be stored in resistant glass or polyethylene bottles. If more pure water is required, this requirement is stated in the individual methods.

Carbon dioxide-free water may be prepared by boiling and cooling demineralized water immediately before use. An equally effective means of removing carbon dioxide is bubbling pure nitrogen in the water. Also, some ion-exchange cartridges will remove dissolved carbon dioxide.

The pH of carbon-dioxide free water should be between 6.2 and 7.2.

Ammonia-free water may be prepared by passing distilled water through a mixed-bed ion-exchange resin.

Standard solutions

The concentrations of standard solutions are indicated as the weight of a given element equivalent to, or contained in, 1 mL of solution. The strengths of acids and bases are given in terms of molarities or normalities.

Nonstandard solutions

The concentrations of nonstandard solutions are indicated in terms of the weight of solute dissolved in a solvent and diluted to a given volume. Unless specifically indicated otherwise, the solvent is demineralized water of required purity. Designation of concentration in terms of percent is not used.

Accuracy of measurement

Within the methods, significant figures are utilized to define the accuracy of weights and measures. Weighings will be accurate to the last figure shown; for example, mass designated as 4.532 g must be weighed accurately to ± 0.0005 g, whereas a mass designated as 4.5 g must be weighed accurately to only ± 0.05 g.

Required accuracy for measurement of volume in the analysis and preparation of reagents is shown similarly. Standard solutions are always prepared in and measured from volumetric glassware. The significant figures given for such measurements are in practical agreement with the tolerance limits for volumetric glassware used; for example, "Add 5.0 mL of reagent" requires the use of a volumetric pipet for the addition, but "add 5 mL" requires the use of a serological pipet; "dilute to 1,000 mL" requires the use of a volumetric flask, but "dilute to 1 L" permits the use of a graduated cylinder.

Test-sample volumes less than 5 mL should be avoided, if at all possible, because the calibration of 1- and 2-mL pipets is not as precise as that of the larger-volume pipets. Less error is incurred if a suitable sample dilution is prepared and part of this dilution taken for the test sample. Although the glassware is calibrated to deliver a specific volume at 20 °C, the error in measurement incurred by pipetting samples at room temperature is insignificant for water analysis. One gram of pure water is contained in 1.002 mL at 20 °C and in 1.007 mL at 38 °C; the maximum error in volume that will result from those temperature differences is only 0.5 percent. Brine samples should be brought as near to 20 °C as possible before making dilutions for analysis.

The concentration of some inorganic constituents in a water sample often will exceed the working ranges as recommended in the application section of each method. For example, sodium in brines will exceed the recommended range several fold. Dilution is normally used to bring the concentration of any of these constituents into the appropriate range. This procedure with proper technique is satisfactory for dilutions of 1 to 1,000. The following techniques must be observed: A volumetric pipet (Class A) smaller than 5.0 mL must never be used and all volumetric flasks used must be Class A.

References

Rosin, Joseph, 1955, Reagent chemicals and standards: New York, D. Van Nostrand, 561 p.

U.S. National Bureau of Standards, 1959, Testing of glass volumetric apparatus: U.S. National Bureau of Standards Circular 602.

Analytical Techniques

Gravimetry

Principles

Gravimetric determinations are based on the accurate measurement of the mass of a chemical compound of known composition and purity. The trend in modern analytical laboratories is away from the long, tedious, time-consuming gravimetric methods and toward faster instrumental techniques, particularly techniques that permit simultaneous determination of several constituents. Nevertheless, some determinations can be performed only gravimetrically. These include the determinations of the various forms of dissolved and suspended solids in a water sample.

Analytical balance

An analytical balance is an essential part of every gravimetric method. For many years, the balance commonly used for this purpose is the single-pan, direct-reading type, capable of measuring the mass of an object to within 0.1 mg. In order to maintain this sensitivity, great care must be observed in the use and maintenance of the balance. The balance must be located apart from the chemical laboratory, in a room free of laboratory fumes and strong drafts. The balance must be placed on a vibration-free stand, table, or shelf. Cleanliness is exceedingly important, and any material spilled in the balance case must be cleaned up immediately. Objects to be weighed must not be handled with the bare hands, but only with ivory-tipped forceps or platinum-tipped tongs.

Cleaning the balance thoroughly periodically and, at each time, checking its calibration is advisable. Weights conforming to Class S tolerances are satisfactory for routine water-analysis applications.

No chemicals are ever placed directly on the balance pan for weighing. At the very least a tared weighing paper or aluminum pan is used. Most commonly the material to be weighed is contained in a porcelain or platinum crucible or dish, or in a glass weighing bottle.

Increasingly, electronic analytical balances are used. Because they immediately read the weight to 0.1 mg (or even to 0.01 mg), they are rapid and extremely accurate. Because most weights are determined by differences, electronic balances are easy to use and accurate for determining solids as well as weighing of primary standards. However, these balances require calibration more frequently than do non-electronic types. The following procedure is recommended:

1. Allow balance to warm at least 10 min.
2. Locate the calibration control on your balance and zero the balance.
3. Place weights on the pan to the total capacity of balance. If the balance does not read the same as the weight on the pan, turn the calibration control until it does.
4. Remove the weights from pan and again zero the balance.
5. Repeat steps 1–4 until the balance gives the proper reading. Dual-range balances need to be calibrated separately and will have separate controls.

Balances are more and more being used in conjunction with computers or their own microprocessors for routine determinations. In these cases, weights are printed out and calculations made so analytical data are transmitted directly to a data base with no manual data handling needed.

Accuracy

Gravimetric determinations can be among the most accurate of all quantitative determinations; they are time consuming, however. In quantitative gravimetric measurements of the solids content of water samples, the uncertainties about the composition of the material being weighed usually exceed the uncertainty involved in determining its mass.

Titrimetry

Principles

Titrimetric analytical determinations are based on the reaction of an accurately measurable volume of a solution of known concentration with an exact equivalent amount of the substance being determined. The process of adding reagent solution to react with the sample is known as titration, and the reactant added during the course of the titration is known as a standard solution. Titrimetric determinations are inherently simpler than gravimetric determinations, and hence are usually preferred where simplicity, ease, and speed of analysis are important. Their sensitivity and accuracy can approach those of careful gravimetric measurements.

To be suitable as a basis for a titrimetric determination, the chemical reaction involved must proceed rapidly to completion with no side reactions. The reaction between a strong acid and a strong base is a good example of an ideal reaction for a titrimetric determination. The titration of the anion of a weak acid with a strong acid does not involve an ideal reaction, but the reaction does proceed to an identifiable point of completion. Such a reaction is used to determine the alkalinity of water samples, wherein the carbonate and bicarbonate anions are titrated with standard acid until poorly dissociated carbonic acid is formed.

In addition to a straightforward chemical reaction, an abrupt change of some property of the solution must occur at the equivalence point of the titration. This may be a change in hydrogen-ion concentration, a sharp increase in the concentration of one of the titrant ions, a change in the electromotive potential, or even a change in the electrical conductivity of the solution. This abrupt change may sometimes be made apparent by adding to the system a color-change indicator solution that changes color abruptly when the reaction is complete at the equivalence point. When the equivalence point is accompanied by a rapid change of pH, an indication of its occurrence may be monitored with a glass electrode. Such titrations are called electrometric titrations.

Standard solutions

The standard solution used in titrimetry must be simple to prepare and preferably stable for a comparatively long time to avoid the need for frequent restandardization. Quite commonly, the standard solution is not prepared directly, but is prepared at a concentration very close to that desired and then standardized by titrating an accurately measured amount of a primary standard. The primary standard must be of high purity, or at least of accurately known purity, must be stable, and easily dried and weighed. An example of a good primary standard substance is the sodium carbonate used to standardize the strong acid used in neutralization titrations. Many other primary standards are useful for various purposes; these standards are available, on specification, from chemical supply companies. The National Bureau of Standards supplies certified primary standard substances for the common titrimetric applications.

Factor-weight computations

The concentration of the titrant may be adjusted so that when a sample of given size is taken for analysis, the volume of titrant in milliliters is in simple proportion to the concentration of the sought constituent, for example, in milligrams per liter. Some time is involved in initial adjustment of the titrant concentration, but time is saved in the long run when many analyses are performed. Simplifying computations in this manner also minimizes arithmetic error in handling the data.

Automated titrations

Systems are available that automate the entire process of a titrimetric determination including the initial measurement of a sample aliquot into a titration vessel. Titrations involving colorimetric as well as electrometric detection of the equivalence point may be automated.

The samples are placed in a revolving tray or moving platform and are sequentially moved into position for titration. As each titrant is completed, a printer records the sample number and the exact volume of titrant added. Such automatic titrators speed the analytical process by freeing the analyst for other duties while the titrations are being carried out. They also have the advantage of duplicating equivalence-point conditions for all samples, avoiding individual judgment on the part of the analyst. Such automated equipment is particularly desirable when a great many routine samples are to be analyzed.

The trend in titrimetric titrations is also toward microprocessors, which automatically calculate and transmit the concentration of desired constituents. Understanding the chemistry behind these reactions is increasingly important to properly program these sophisticated data-handling systems—now used in conjunction with both colorimetric and electrometric detection of equivalence point.

Atomic absorption spectrometry

Basic principles

When a beam of radiant energy is passed through a cloud of atomic vapor, certain very specific wavelengths characteristic of the element(s) in the vapor are absorbed. This principle forms the basis of a very sensitive and highly selective method of analysis for most metallic elements (Walsh, 1955).

Each element absorbs energy at a series of wavelengths that constitutes the unique atomic spectrum of that element. Selectivity is achieved by careful choice of the wavelength of radiant energy passed through the sample. Because atomic absorption occurs in extremely narrow (approximately 0.002 nm) intervals of the electromagnetic spectrum (Robinson, 1975), a wavelength can usually be selected that is absorbed by only one constituent of a sample.

Under ideal conditions, the extent of absorption at a specific wavelength is related to the concentration, c, of a given element in the vapor and to the length, b, of the path that the beam traverses through the vapor, according to Beer's Law:

$$A = a\ b\ c \qquad (1)$$

In this equation, a is a constant of proportionality and A, the absorbance, is defined as:

$$A = \log P_o/P \qquad (2)$$

where P_o is the radiant power of the unabsorbed beam (measured in the absence of atomic vapor) and P is the radiant power of the beam after it has passed through the atomic vapor.

Instrumental principles

Instrumentation for atomic absorption spectrometry consists of the following components, listed in the order of their function in the instrument:

(1) Source of radiant energy
(2) Sample chamber
(3) Wavelength selector
(4) Detector of radiant energy
(5) Readout device (information processor)

A brief operational description of each component follows.

Radiant energy source

The source of radiant energy must produce intense radiation at the exact wavelength absorbed by element to be determined. If Beer's law is applied, the width of the emission lines in the spectrum of the source must to be narrower than the absorption lines of the element in the sample. This is achieved by exciting radiation from low-pressure vapor of the element. Two types of lamps are commonly used to produce atomic radiation: the hollow cathode lamp (HCL) and the electrodeless discharge lamp (EDL).

The HCL consists of a glass or quartz tube containing a small metallic cup that is lined with

(or made of) the element to be determined. This cup is given a negative electrical charge so that positively-charged ions of a low-pressure fill-gas, such as argon, are accelerated toward it, releasing metal atoms when they strike the cup. These atoms are struck by other fill-gas ions, imparting energy that raises them to excited atomic states. Characteristic atomic spectra are emitted by these excited atoms when they return to the ground (normal) electronic state.

In an EDL, a small amount of the element to be determined is sealed under vacuum in a small quartz bulb, which is surrounded by a coil. When a radio-frequency alternating current is passed through this coil, its energy is imparted to the metal vapor, causing it to emit the characteristic atomic spectrum of the metal.

Either type of lamp is capable of producing the spectrum of only one element (a few mixed-element lamps are made that can produce spectra of 2 to 5 elements, but these are usually less desirable due to lower intensity). HCL's tend to be less intense than EDL's and have relatively limited lifetimes, even if infrequently used. EDL's are generally preferred for those elements for which they are available.

The radiant-energy beam from the source lamp is usually modulated, either by "chopping" the beam with a rotating mechanical shutter or by modulating the power supplied to the lamp. This modulation enables the detector to distinguish the source beam from unmodulated radiation produced in the flame or furnace.

Sample chamber

Atomic vapors may be produced by aspirating metal salt solutions into flames, by vaporizing solutions in electrically-heated graphite tubes, or by chemically producing volatile metal hydrides that are decomposed to atoms in quartz tube-furnaces. Only one commonly determined element, mercury, is volatile enough to produce measurable atomic vapor at room temperature. These methods are designated "flame," "electrothermal," "hydride-generation," and "cold-vapor" atomic absorption spectrometry, respectively. The principal factors to be considered in selecting among these methods are the speed and ease of analysis, the detection limit required, and the quantity of sample available.

For flame atomic absorption, the sample is converted to an aerosol in a nebulizer and mixed with fuel and oxidant gases. This mixture is burned in a long, narrow burner that provides a long path-length for the radiant energy beam. Because the sample is greatly diluted by fuel and oxidant gases, detection limits by flame atomic absorption are generally limited to 10–100 micrograms of metal per liter of solution. Because the sample quickly passes through the flame and is lost, aspiration is continuous during the analysis time. Therefore a relatively large volume (several milliliters) of sample is required. Operational ease and relatively fewer interferences make flame atomic absorption the fastest and simplest of the methods.

In electrothermal atomic absorption, a few microliters of sample are deposited into a small graphite tube at room temperature. The tube is then electrically heated through a pre-programmed cycle of four distinct steps:

1. Evaporation of solvent (approx 120 °C)
2. Charring of volatile (organic) matter (several hundred degrees)
3. Atomization of the metal at high temperature and determination (800–2500 °C)
4. Cleanout at very high temperature (3000 °C)

This process has until recently been subject to so many interferences that the method of standard additions has almost universally been required. Recently, basic studies of the nature and origin of these interferences have lead to some revised techniques, that help to optimize the rate of vaporization and, thus, have reduced interferences significantly. Among these new techniques are vaporization of the sample on a small graphite platform (L'vov platform) mounted inside the furnace and addition of chemical matrix modifiers.

Elements such as arsenic, selenium, antimony, and tin are usually converted to gaseous metal hydrides, that are introduced into small quartz tube furnaces where the hydrides decompose to produce atomic vapor. Mercury is reduced to the elemental state and swept by a stream of inert gas into a cool quartz tube in the sample chamber.

Wavelength selector

After the radiant energy beam has passed through the sample, a monochromator is used to select only one of the characteristic lines of the element being determined. Monochromators use diffraction gratings to spread the beam into a spectrum and from this spectrum an exit slit selects one wavelength for analysis. That wavelength may be in the visible (400–700 nm) or ultraviolet (200–400 nm) region of the spectrum.

For most elements, a principal wavelength and possibly one or more alternate wavelengths are specified in approved methods. The selected principal wavelength is very intense in the source-lamp spectrum, strongly absorbed by the atomic vapor, and free from interferences by other elements commonly found in water samples. Alternate wavelengths chosen for lower sensitivity may be used for more concentrated samples, *if specified in the approved method.*

Instrument performance is affected by slit width. A slit too narrow may degrade a detection limit because too little energy passes to the detector, and a slit too wide may result in noisy signals or in erronous readings due to excessive background radiation or excessive curvature in the calibration.

Detector

The detector is usually a light-sensitive vacuum tube called a photomultiplier. When a bias voltage of several hundred volts is applied to a photomultiplier, it generates an electrical current proportional to the power of radiant energy incident upon it. These devices are very delicate and should never be exposed to strong room lights, especially when the bias voltage is on. Such an exposure will produce "noisy" readings for several days thereafter or may permanently damage the detector.

Information processing

Electronic circuitry, often including microprocessors, is employed to convert the P_o and P values registered by the photomultiplier into human- or machine-readable indications of absorbance, or (by comparison to standard solutions of known concentration) into actual concentration readings. In older instruments, these readings were registered on chart recorders or on panel meters. Modern instruments provide digital readout, either on a display panel or on a printer, and may be able to transmit readings to computers.

Readings for flame atomic absorption are usually steady signals, which are averaged over a period of 0.5 to 5 seconds as appropriate to the noisiness of the signal. In contrast, electrothermal atomic absorption signals are transient, rising to a peak and decaying back to zero in only a few seconds. Such signals are measured by either the height of the peak, or by integrating the area under the peak. The choice will depend on the relative precision and accuracy obtained by the two methods, which are governed by such factors as the sharpness of the peak and the shape, position, and intensity of the background absorption signal.

Analytical procedures

Direct

The sample may be analyzed by direct introduction into the flame or furnace, if the concentration of the element to be determined is great enough, and the interference effects are small enough. Concentration is calculated by comparison of the sample's absorbance to the absorbances of a series of standard solutions. This is performed either manually by constructing an analytical curve, or electronically by "curve fitting" in a microprocessor-controlled instrument. Although Beer's Law predicts a straight-line relation between absorbance and concentration, some curvature is often found, and is tolerable up to a point.

Chelation-extraction

It is possible to react many metal ions with an organic chelating reagent, such as ammonium pyrrolidine dithiocarbamate (APDC) or 8-hydroxyquinoline and then extract the resulting chelate into a water-immiscible solvent such

as methyl isobutyl ketone (MIBK), where the concentration of the metal to be determined is too low for direct measurement, or where serious interferences are present. If, as is typically the case, 100 mL of a water sample is extracted with 10 mL of MIBK, the concentration of metal ions in MIBK is approximately 10-fold greater than in the original sample. In addition, detection limits are generally improved in organic solvents, so the actual improvement in detection may be actually much greater than 10-fold.

Chelation-extraction can also be used to eliminate interfering substances which are not extracted under the conditions chosen. On the other hand, some substances in the sample may interfere with the chelation reaction by reacting preferentially with the chelating agent.

APDC is used in several of the chelation-extraction procedures in this chapter. Although it may be obtained commercially, a somewhat superior product may be prepared in the laboratory. The preparation is simple, rapid, and requires little equipment.

CAUTION: The reagents and reactions are potentially hazardous. Safety gloves and safety glasses must be worn, and a well-ventilated hood must be used in all steps of the procedure. Reactions that occur release heat and must be performed in an ice bath with constant stirring.

Apparatus

Condenser, reflux, with ground glass joint 24/40.
Flask, Erlenmeyer, 1000-mL capacity with ground glass joint 24/40.
Funnel, Buchner, 16-cm diameter.
Funnel, separatory, 250 mL.
Magnetic stirrer.

Reagents

Ammonium hydroxide, 8 N: In a well-ventilated hood, dilute 133 mL conc NH_4OH (sp gr 0.90) to 250 mL with demineralized water and mix.
Carbon disulfide, reagent-grade: **CAUTION: Vapor is very toxic and can be sorbed through skin. Flammable.**
Ethanol, 95-percent: Denatured ethanol may be used.
Pyrrolidine, practical: **CAUTION: Vapors are very toxic and liquid causes burns. Highly flammable.**

Procedure

1. Dissolve 135 mL pyrrolidine, with continuous mixing, in 300 mL ethanol in a 1000-mL Erlenmeyer flask.
2. Attach the reflux condenser to the flask and place in an ice bath. Cool for 30 min. Stir solution continuously, with a magnetic stirring device.
3. Place 90 mL CS_2 in a 250-mL separatory funnel and slowly add the CS_2 dropwise (2 to 3 drops per second) through the condenser. Addition of the CS_2 produces a strong warming effect; therefore, cool the flask with ice at all times and stir continuously. After the CS_2 has been added, cool the mixture for an additional 15 min.
4. Add 225 mL 8 *N* NH_4OH. APDC crystals will form rapidly. Chill the mixture for at least 1 h. For maximum yield, place the flask in a freezer for several hours.
5. Assemble a Buchner funnel, fitted with a Whatman No. 41 paper, and vacuum-filtering flask. Rinse the funnel with several milliliters of chilled ethanol.
6. Dislodge the APDC crystals from the walls of the flask with a glass rod. Decant the solution and APDC crystals into the funnel, and apply vacuum.
7. Rinse the flask with a small portion of chilled ethanol and pour over the APDC in the funnel. Repeat this procedure until the filtrate appears clear. Rinse the APDC twice more with chilled ethanol.
8. Dry the APDC by continuing the vacuum for about 1 h.
9. Remove the APDC from the funnel, place in an amber bottle, and store in a refrigerator. The yield is approx 180 g, about 75 percent of theoretical.

Standard additions

The method of standard additions is a frequently used analytical technique when certain

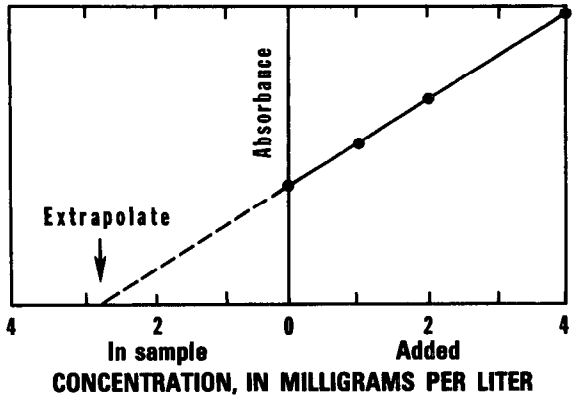


Figure 1.—Example of standard-addition method

types of interferences are present, or are suspected because of unfamiliarity with the nature of the sample or the method of analysis. It is carried out by adding equal volumes of a blank and three different known standard solutions of the metal to be determined to four aliquots of the sample. The absorbance of each of these solutions is plotted on the vertical axis of a graph whose horizontal axis is concentration of metal added (to the right) and concentration of the unknown (to the left). An example is plotted in figure 1. The concentration of the unknown solution is determined by extrapolating the line through the experimental points to the horizontal axis. This is clearly too time-consuming a procedure for high-volume routine analysis, because four measurements are required to produce a single analysis.

Matrix effects, ionization interferences and chemical interferences may be detected and/or overcome by the method of standard additions, but *two very important limitations must be noted carefully*:

(1) The method of standard additions is *not* effective insurance against errors due to background absorption or spectral lines interference;
(2) A linear calibration curve throughout the entire concentration range utilized is *absolutely required.*

Methods for detecting and removing background effects and spectral line interferences are discussed in a later section. Nonlinearity can be checked by analyzing the sample under several successive dilutions from full concentration down to the detection limit of the method.

Interferences

Numerous types of effects can destroy the ideally simple relationship between absorbance and concentration. It is important that the analyst understand the basic nature and cause of each of these effects, so that potential sources of error can be anticipated and avoided.

Ionization effects

A significant fraction of the atoms may be ionized if excessive heat is applied to a vaporized sample. Because ions do not absorb at the same wavelength as neutral atoms, ionization will cause a decrease in the intensity of the absorption signal. No systematic analytical error will result, as long as this decrease occurs equally in the calibration standards and in the sample. If, however, a particular sample contains a large amount of some easily-ionized element, an excess of electrons will be produced. These excess electrons will repress the ionization equilibrium of the analyte metal, leading to an enhancement of the absorption signal in that particular sample. A common example is the enhancement of the potassium signal in samples that contain high concentrations of sodium. Elements on the left side of the periodic table (notably alkali and alkaline earth metals) tend to be the most easily ionized, and are most subject to ionization effects.

Ionization interferences are controlled in one of two ways; first, by keeping flame or furnace temperatures as low as possible when measuring easily-ionized elements, or secondly, by adding a large excess of an easily-ionized substance (such as cesium) to both standards and the samples, so that the ionization equilibrium is entirely driven toward the neutral atom in all samples and standards.

Chemical effects

Some metals tend to form thermally-stable compounds when heated in flames or furnaces. These compounds prevent the formation of atoms in the sample chamber of the spectrometer, and thus lead to erroneously low absorbance

readings. The reduction of the absorbance of calcium when phosphate or silica is present at high concentration is a classic example of a chemical interference because calcium phosphate and calcium silicate are dissociated only at very high temperatures. A "releasing agent" (something that reacts with these anions more strongly than does calcium) will liberate calcium by tying up the interfering anions. Strontium and lanthanum are commonly used releasing agents for calcium and magnesium. Alternatively, a hotter flame may be able to thermally dissociate the stable compound.

Another example of chemical interference is the formation of refractory (i.e., heat-stable) oxides and carbides by certain heavy metals. In this case, the use of hotter flames will at least partially dissociate these compounds. Table 4 shows the temperatures attained in commonly used analytical flames. The nitrous oxide-acetylene flame is frequently used to dissociate thermally stable compounds such as calcium phosphate and refractory oxides. Oxide-forming metals may benefit from the use of fuel-rich flames, so as to decrease the availability of oxygen atoms. Carbide-forming elements, on the other hand, may best be determined in non-hydrocarbon flames such as air-hydrogen, or in the presence of excess aluminum as a releasing agent (Price, 1979).

Table 4.—Temperatures of premixed flames

Oxidant	Fuel	Temperature (degrees Celsius)
Air	Natural gas	1700-1900
Air	Hydrogen	2000-2050
Air	Acetylene	2175-2400
Nitrous oxide	Acetylene	2600-2800

Matrix effects

Although both of the interferences previously discussed might be called "matrix effects", this term is usually reserved for the simple physical effect of viscosity and surface tension on the efficiency of the nebulization process in flame atomic absorption. Typical of these effects is the general decrease in absorbance signals which occurs with increasing acidity of the sample. Acid affects the viscosity and surface tension of the sample, and therefore the rate at which the sample is nebulized into the flame. The best way to combat such interferences is to calibrate using standards that have the same acidity as the samples to be analyzed. Unequal amounts of dissolved solids in samples and standards also may cause errors in the analysis due to different nebulization of such solutions by the atomizer. Again, this may usually be controlled by matching the density or viscosity of samples and standards, or by adding a noninterfering salt to the standards. Where matrix effects are severe or the matrix is completely unknown, the method of standard additions is highly recommended.

Spectral-line effects

Spectral-line interference occurs when there is overlap between the spectral line of the element sought and that of another element in the sample. Because wavelengths for analysis are selected to avoid overlapping lines, this problem seldom arises. However, when a nonanalyte element is present at very high concentration, its lines are broadened and may overlap the line of the sought-for element. The analyst needs to be alert to the possibility of errors due to interference of this type in samples of unusual or unknown composition. One means of detecting spectral-line interference is to perform the determination at two different wavelengths. Spectral-line interference is suspected when determinations at two wavelengths yield different concentration values.

Background absorption

Background absorption is a collective term used to describe the combined effects of flame absorption, molecular absorption, and "light scattering" by particles in the light path. Each of these effects results in a broad, flat absorption band which is superimposed on the atomic line absorption, resulting in erroneously high absorbance readings. Background absorption is particularly severe in the graphite furnace. This effect is eliminated by use of a background

correction device which automatically subtracts the "off-peak" absorbance, or background, from the "on-peak" absorbance.

The most common type of background corrector is the deuterium-arc (a continuum, or broad-spectrum source). Light from this continuum source is passed through the flame or furnace simultaneously with the hollow cathode or electrodeless discharge lamp (sharp-line source). Because the lines in atomic spectra are so narrow, the absorbance measured by the continuum source is caused almost entirely by background, whereas the sharp-line source measures both atomic and background absorption. The atomic absorption is computed by subtraction of the background from the atomic-source absorbance.

A more recent development in background correction is the Zeeman Effect background corrector. When a body of atomic vapor is subjected to a strong magnetic field, a typical atomic absorption line is split into three components, one at the original wavelength and one on either side of it. These absorption lines are polarized, with the center one having opposite polarization from the two lines to the sides. Thus, under one condition of polarization of the source beam, the atomic vapor does not absorb and only background absorption is measured at the center-line wavelength; whereas, under opposite polarization both the atomic vapor and the background absorption are measured. Some loss of sensitivity is usually experienced, with a corresponding degradation of the detection limit. Also, some atomic lines give atypical splittings which do not lead to useable results. However, in most cases Zeeman spectrometers are capable of handling extremely high backgrounds due to very "dirty" matrices. Although available for flame atomic absorption, the Zeeman Effect is primarily applied to electrothermal atomic absorption.

Automation techniques

Autosamplers for both flame and electrothermal atomic absorption spectrometers are commercially available. These devices are microprocessor controlled and, when used in conjunction with a printer, permit unattended operation for 40 to 60 samples. A few more advanced autosamplers have the capability to perform standard additions and (for furnaces) to introduce matrix modifiers with each sample.

Hydride generation may be automated using continuous-flow systems to add reagents in sequence and to provide the required heating and reaction-time delays. The volatile metal hydrides so generated are separated from the sample solution in a packed separator column, and are then swept into an electrically-heated quartz tube furnace by a stream of inert gas. The cold-vapor method for mercury may be similarly automated.

A significant recent advance in automation of atomic absorption is flow injection analysis (Betteridge, 1978; Wolf and Stewart, 1979). Under microcomputer control, a few microliters of sample are injected by means of a loop sampling valve into a pumped stream of a carrier liquid which flows continuously into the nebulizer of a flame atomic absorption spectrometer. The "plug" of sample disperses in the carrier stream, producing a transient signal reminiscent of that observed in a graphite furnace analysis or chromatography. The area under this peak is integrated and compared to standards for quantitation. Principal advantages of this method are (1) speed (as many as 400 determinations per hour) and (2) increased precision due to the excellent control of the aspiration process afforded by precision pumping of the sample stream.

References

Beaty, R. D., 1978, Concepts, instrumentation and techniques in atomic absorption spectrophotometry: Norwalk, Conn., The Perkin-Elmer Corporation, 49 p.

Betteridge, D., 1978, Flow injection analysis: Analytical Chemistry, v. 50, p. 832a-846a.

Dean, J. A., and Raines, T. C., 1969, Flame emission and atomic absorption spectrophotometry v. 1: New York, Marcel Dekker, 435 p.

Fernandez, F. J., Myers, S. A. and Slavin, W., 1980, Background correction in atomic absorption utilizing the Zeeman Effect: Analytical Chemistry, v. 52, p. 741-746.

Kaiser, M. L., Koirtyohann, S. R., Hinderberger, E. J., and Taylor H. E., 1981, Reduction of matrix interferences in furnace atomic absorption with the L'vov platform: Spectrochimica Acta, v. 36 B, p. 773-783.

Price, W. J., 1979, Spectrochemical analysis by atomic absorption: London, Heyden, p. 134.

Robinson, J. W., 1975, Atomic absorption spectroscopy, 2nd. ed.: New York, Marcel Dekker, p. 20.

Walsh, A., 1955, The application of atomic absorption spectra to chemical analysis: Spectrochimica Acta, v. 7, p. 108-17.

Wolf, W. R., and Stewart, K. K., 1979, Automated multiple flow injection analysis for flame atomic absorption spectrometry: Analytical Chemistry, v. 51, p. 1201-1205.

Atomic emission spectrometry

Principles

Emission phenomenon

When a metal atom in the gas phase ground state (M) is heated in an exitation source, energy is supplied to the atom via collision with high-temperature atoms and molecules resulting in transitions of electrons within the metal atom to higher energy states. The excited atom M* can then lose energy by emission of a photon. The process can be represented thus:

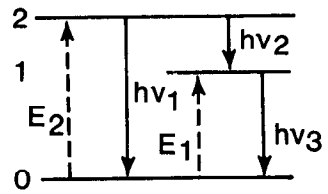
$$M + \text{energy} \rightarrow M^* \rightarrow M + h\nu$$

The energy of each of the emitted photons, $h\nu$, equals the difference between the energies in the higher and lower energy levels (fig. 2). Each transition emits a photon at a wavelength given by $\lambda = c/\nu$, and each element has a characteristic pattern of emission wavelengths. In the simplified example, (fig. 2) the population of atoms in the excitation source can be excited to either energy level one or two. Emission can occur by transition from energy levels one or two to the ground state, or by an intermediate transition from level two to one. Usually, one or more transitions ending in the ground state is the most probable, resulting in one of the characteristic emission wavelengths (lines) of greatest intensity.

Emission from ions occurs in a similar way, but because the energy levels are different from those of the atoms, the characteristic emission wavelengths are normally different as well.

Quantitative analysis by emission

In order for the emission phenomenon to be used in quantitative chemical analyses, the following are necessary: (1) the sample must be atomized (constituents of interest converted to atoms or ions in the gas phase) and the resulting atoms or ions excited; (2) the resulting characteristic emission lines must be spectrally separated and their relative intensities measured by a suitable dispersion-detection system (spectrometer or spectrograph); and (3) the resulting intensities must be compared with standards of known elemental composition. Solid samples are usually analyzed by arc or spark exitation sources that atomize and excite elements directly from the sample. Solutions are generally analyzed with flame or plasma exitation sources into which the sample is aspirated. In both cases, one or more elements can be quantified simultaneously from the emission lines.



$E_2 = h\nu_1$

$E_2 = h\nu_2 + h\nu_3$

$E_1 = h\nu_3$

Figure 2.—Energy level diagram

The fraction of sample atoms excited varies exponentially with the excitation-source temperature—the Boltzmann distribution (Mavrodineanu and Boiteux, 1965) being a good approximation of the fraction if the source attains or approaches thermodynamic equilibrium. Thus, the higher the temperature of the excitation source, the greater the emission intensity for a given atomic concentration in the source. Moreover, the atomization (formation of atoms in the source) of many sample media is more complete at higher temperatures: an increasing concentration of atoms or ions in the exitation source results from increasing temperatures. Although the analytical sensitivity might seem to increase and the detection limit decrease almost without limit by increasing the temperature of the excitation sources at higher temperatures, several other phenomena occur that limit the benefit of higher source temperatures: ionization of the sample atoms, which

removes atoms from one emitting population to another, becomes increasingly important; the spectrum becomes more complex as more upper-level lines are excited; and, perhaps most importantly, the source background emission also increases rapidly.

The principal advantages of atomic emission are low analytical detection limits for many elements, simple instrumentation, good specificity and speed of analysis, and adaptation to simultaneous, multi-elemental analysis. The principal limitation is that atomization-excitation conditions can simultaneously be optimized to a degree satisfactory for quantitative analysis for only a limited number of constituents. This limitation results about from the interdependence of the atomization and excitation processes. Conditions to optimize one process may cause interferences in another. For example, with relatively low-temperature sources, which minimize ionization and background, the population of excited atoms is low and the analytical sensitivity and detection level are poor relative to those in higher temperature sources. With high-temperature sources, the population of excited atoms is large, but high background and complex spectra are produced that can adequately be resolved only by a high-resolution spectrometric system. The other serious limitation is compound formation in the atomization-exitation source, an effect that reduces the atomic population in the source and places an upper limit on sensitivity for many elements.

Types of excitation sources

Flames

The chemical flame is the oldest emission source, dating from the 1860's, and it is still in wide use today. Various types of chemical flames and burner designs have been developed for analytical work. As emission sources, flames have much to offer. They are simple and inexpensive to operate, and the temperatures developed in the flames are adequate to excite 10 to 20 metals, enabling analyses in water at the milligram-per-liter concentration range or less. The temperatures of the most commonly used

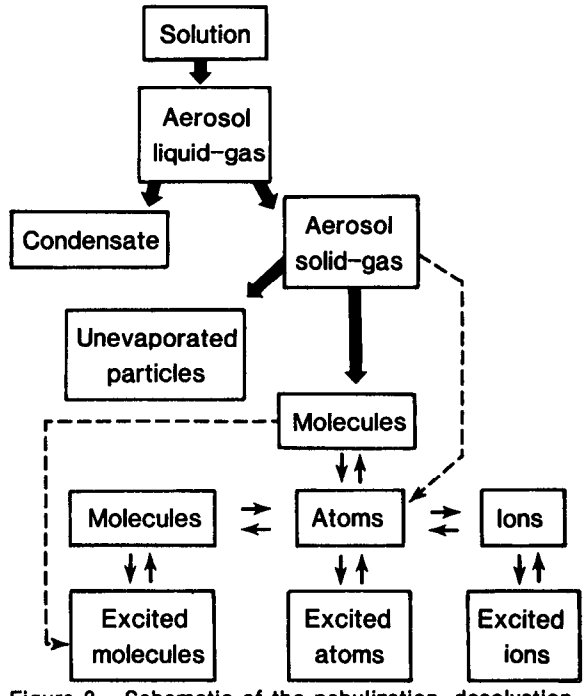


Figure 3.—Schematic of the nebulization, desolvation, atomization, and excitation processes

flames range from the 2,000 to 3,000 K; this range results in good analytical sensitivity for elements that have relatively low excitation energies and that are atomized to an appreciable extent in the flame, that is, those having no strong tendency toward compound formation.

Flames are used most for analysis of liquid samples, either aqueous solutions or organic solvents. Samples are introduced into the flame through a nebulizer, which converts the sample solution into a fine mist. Once in the flame, several processes occur in rapid succession: desolvation, atomization, and excitation, as illustrated in figure 3. Many nebulizer and burner designs have been developed. These are extensively reviewed by Mavrodineanu and Boiteux (1965).

The production of gas-phase metal atoms from the sample depends initially on the thermodynamics and kinetics of the desolvation-atomization processes. Commonly only a small fraction of the sample reaches the flame. Additional atoms can be lost from the population of emitting atoms by compound formation with flame gas products and by ionization, but ionization is a limiting factor for only a few elements

that are easily ionized in relatively hot flames. By far the most important loss mechanism is compound formation of analyte atoms with flame gas radicals. Many elements form stable compounds in the flame, notably metal monoxides. In the general equilibrium:

$$M+O \rightleftharpoons MO$$

the forward reaction is exothermic, so an increase in temperature shifts the equilibrium toward the free metal atom if the oxygen concentration remains the same. A decrease in the oxygen concentration also shifts the equilibrium toward the free metal atom. Because one normally has little control over the temperature in chemical flames, the more common approach to shift the equilibrium is to lower the free-oxygen content of the gases. One means of doing this, especially in hydrocarbon flames, is to make the flame fuel rich. The slight drop in flame temperature under fuel-rich conditions does not reduce the exitation efficiency substantially so a net gain in free metal atom is achieved. Extracting the constituents of interest from aqueous solution into organic solvents reduces compound formation by reducing source cooling from the aqueous solvent and by improving the nebulization and desolvation efficiencies.

Flames also have some important limitations for use as emission sources: (1) temperatures much above 3,000 K cannot be obtained with the usual fuel-oxidant combinations; for many elements with high excitation energies this temperature is too low to excite a population of atoms adequate for good analytical sensitivity; (2) the chemical environment of the flame fosters compound formation which effectively removes metal atoms of interest from the atomic emission process; and (3) considerable background emission may be present in certain spectral regions (for example, the OH emission between 300 and 350 nm and the C_2, CN, and CH emissions from hydrocarbon-fueled flames). Despite these limitations, flame atomic emission remains one of the simplest and most sensitive analytical methods for easily excited elements that do not form highly stable compounds at high temperatures, such as alkali, alkaline earth, and several transition elements.

Direct-current arc

The direct-current (d-c) arc discharge (Slavin, 1971) is a widely used spectrochemical excitation source and is almost always employed with a spectrograph or multichannel spectrometer. A high-current, low-voltage discharge is maintained between two electrodes (usually graphite), one containing the sample (usually the anode) and operating in air (free-burning) or in some other gas mixture at atmospheric pressure. Electrodes are most often made from high-purity carbon, or graphite, because of their high-temperature stability, ease of fabrication, and ease of purification.

With a high arc temperature, the analytical sensitivity is high, and low detection limits for most elements result. Due primarily to wandering of the arc on the electrode surfaces during the discharge, the reproducibility of the emission from sample to sample is poor. Consequently, reproducibilities in analyses are seldom better than about ± 20 percent. This makes the d-c arc source better suited to qualitative or semiquantitative analyses, rather than quantitative work. The tremendous sensitivity of this high-temperature source combined with the capability for simultaneous multielement analysis make the d-c arc a very powerful and useful analytical tool despite poor reproducibility.

The d-c arc is used mostly for analysis of solid samples, usually in powder form. Liquid samples can be analyzed by first evaporating the sample to dryness in a cup electrode or by rotating a disc electrode into the liquid sample and then into the arc.

Alternating-current spark

The alternating-current, or radiofrequency, spark discharge is another widely used emission source (Slavin, 1971). It too is almost always employed with a spectrograph or direct-reading, multichannel spectrometer. Although resulting in poorer detection limits than the d-c arc, the alternating-current spark discharge provides a higher degree of reproducibility and can be used for quantitative analysis.

The spark occurs repeatedly over a small area of the sample, and each spark is followed by an

"off" period. As a result of this alternating heating-cooling cycle, the bulk of the sample is not heated to emission so that homogeneity and limited-area studies can be made on solid samples and solutions can be analyzed directly. However, the small amount of sample consumed leads to poorer analytical sensitivity and detection limits compared to other methods.

Conducting samples (for example, metals) are usually ground flat and used as one electrode with a pointed graphite counterelectrode (point-to-plane technique). Powdered samples (conducting and nonconducting) are usually mixed with graphite powder and pressed into a pellet that is used as the plane electrode. Solutions are usually analyzed using a porous-cup (graphite) electrode or a rotating-disc electrode. The former consists of a porous-bottom graphite cup containing the sample solution and a counter-electrode beneath the cup, discharging to the wet bottom of the porous cup. The rotating-disc electrode consists of a rotating graphite disc, the lower edge of which dips into the sample solution and carries it to the spark-discharge region at the top of the disc. Numerous other electrode arrangements have been used, but these two are the most popular.

Direct-current argon plasma (plasma jet)

The d-c plasma jet developed by Margoshes and Scribner (1959) is produced by forcing argon gas through an orifice housing a d-c arc discharge. Liquid samples are drawn into the plasma by an apparatus described by Keirs and Vickers (1977) in which liquid samples are aspirated into a chamber, mixed with argon, and swept through the orifice.

The temperature of the plasma approaches 10,000 K and, in addition to the usual nonionized spectral lines, spectra of ionized atoms are produced and in some situations predominate. The actual temperature of the plasma depends on the arc current, electrode geometry, and gas-flow rates. When gas flow is increased, electrical conductivity rises. This, in turn, results in a higher current and, as a consequence, higher temperatures at the core of the discharge. Often, this effect varies as the composition of samples changes. To overcome problems in analysis caused by these effects, an excess of an easily-ionized cation is usually added to the samples to buffer the ionization, and an internal standard is used for calibration.

Only a small fraction of the sample aerosol particles actually enters the plasma. Because of this and the intense plasma background emission, a high-resolution optical system is needed to achieve high analytical sensitivity. Reednick (1979) has described a commercially available d-c arc plasma jet used with a high-resolving-power echelle spectrometer.

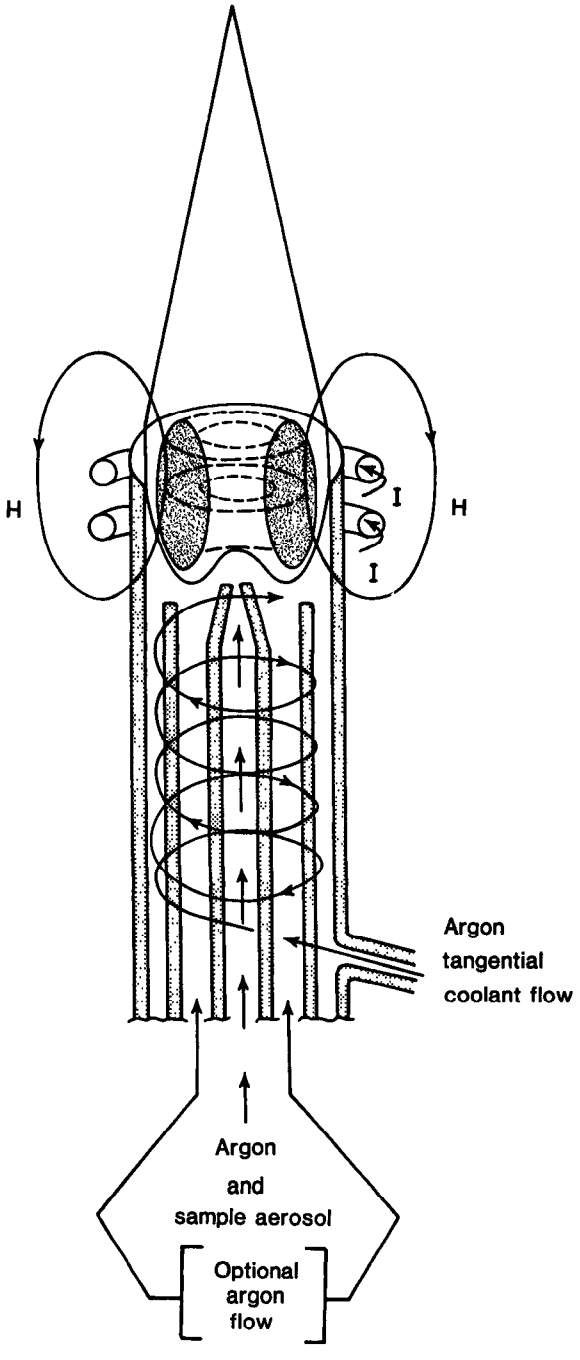
Inductively-coupled argon radiofrequency plasma torch

In recent years, inductively coupled radio-frequency plasma (ICP) torches have been applied for spectrochemical analysis in both emission spectroscopy (Greenfield and others, 1964; Wendt and Fassel, 1965) and absorption spectroscopy. This type of torch was first described by Reed (1961) as a new method of generating a stable plasma at atmospheric pressure.

The equipment for producing an inductively-coupled radiofrequency plasma torch consists of a quartz tube surrounded by a few turns of water-cooled tubular copper coil connected to an induction-heating power generator (fig. 4). One end of the quartz tube is open and the other end receives the gas supply. The gas is heated by the currents induced in the plasma.

The coupling between field and plasma improves as the plasma approaches the coil, causing the plasma to expand. The outer tube prevents the plasma from reaching the coil and causing a short circuit and, simultaneously, thermally stabilizes the plasma. The heat from the plasma is continuously removed by cool argon gas flowing between the outer and middle tubes. A laminar stream of cold argon flowing through the space between the outer and the middle tubes surrounds the plasma, stabilizes the torch, and prevents wall contamination. The inner nozzle permits the injection of an aerosol.

In general, inductively coupled plasmas have many properties in common with d-c argon plasmas. The core temperature for the argon plasma is about 10,000 K. The combination of high-excitation temperature and inert atmosphere provides a highly stable, sensitive, and



relatively interference-free excitation source for solution samples.

References

Greenfield, S., Jones, I. L., and Berry, C. T., 1964, High-pressure plasmas as spectroscopic emission sources: Analyst, v. 89, p. 713-20.

Keirs, C. D., and Vickers, T. J., 1977, DC plasma arcs for elemental analysis: Applied Spectroscopy, v. 31, p. 273-83.

Margoshes, Marvin, and Scribner, B. F., 1959, The plasma jet as a spectroscopic source: Spectrochimica Acta, v. 15, p. 138-45.

Mavrodineanu, R., and Boiteux, H., 1965, Flame Spectroscopy: New York, John Wiley, 285 p.

Reed, T. B., 1961, Induction-coupled plasma torch: Journal of Applied Physics, v. 32, p. 821.

Reednick, J., 1979, A unique approach to atomic spectroscopy-high energy plasma exitation and high resolution spectroscopy. American Laboratory, March, p. 32.

Slavin, Walter, 1971, Emission Spectrochemical Analysis: New York, Wiley-Interscience, 254 p.

Wendt, R. H., and Fassel, V. A., 1965, Induction coupled plasma emission sources: Analytical Chemistry, v. 37, p. 920-2.

←Figure 4.—Plasma torch configuration

Colorimetry

Basic principles

Colorimetric and spectrophotometric methods in analytical chemistry are founded on the conversion of the constituent of interest into a substance whose solution or suspension is strongly colored and, thus, will absorb radiant energy (Sandell, 1959; Skoog and West, 1982).

The basic principle dealing with the absorption of all types of electromagnetic radiation is commonly called Beer's law, but has also been called Lambert-Beer or Bouguer-Beer. Stated mathematically:

$$A = -\log_{10} T = \log P_o/P = abc$$

where

A = absorbance,
T = transmittance (0–100 percent),
P_o = radiant power incident upon the sample,
P = radiant power leaving the sample,
a = absorptivity,
b = light-path length in centimeters, and
c = concentration of the absorbing species.

As this equation shows, the relation between absorbance and concentration or pathlength is linear, and for a fixed concentration of an absorbing substance, the absorbance will vary with path length. No exceptions have ever been found to this relationship. On the other hand, Beer's law also states that absorbance and concentration are directly proportional; many exceptions to this have been found, and these must be considered in the evaluation of the utility of Beer's law in chemical analysis. Such exceptions are usually caused by either chemical effects or instrumental limitations or both. Chemical effects may result because Beer's law only holds for dilute solutions and instrumental limitations result from the use of light of insufficient monochromaticity or from a lack of proportionality between photocell (or equivalent) response and light intensity. For more detailed discussions of Beer's law, the reader is directed to any basic analytical chemistry text (e.g. Kolthoff and others, 1969; Skoog and West, 1980, 1982; Willard and others, 1981).

Instrumental principles

Colorimetry (visible-light range) and spectrophotometry (ultraviolet- and visible-light range, measuring absorption at a single wavelength) can be viewed as the instrumental measurement of the absorption of radiant energy by a solution at a fixed wavelength. Instruments designed and used for this purpose all contain five basic components, not necessarily housed within a single unit. These are (1) a stable source of radiant energy, (2) a device that can be used to control wavelength, (3) transparent containers for the sample and the solvent, (4) a detector that measures radiant energy and converts it to some measurable signal, and (5) a readout device (Skoog and West, 1980; Willard and others, 1981).

1. Radiant energy source–usually a tungsten-filament incandescent lamp for the visible region; hydrogen or deuterium discharge lamps for the ultraviolet region.
2. Wavelength control–a number of devices are available including filters (absorption and interference) and monochromators utilizing either diffraction gratings or prisms.
3. Sample and solvent containers–these must be manufactured from material that permits passage of the radiation of the wavelengths of interest; commonly used materials include quartz, fused silica, silicate glasses, and plastic.
4. Detector–commonly some type of photoelectric device that converts radiant energy into an electrical current, usually a photovoltaic cell, a phototube, a photoconductive cell, or a photomultiplier tube.
5. Readout–typically some kind of meter, a digital readout, or a chart recorder.

Detailed descriptions of the various components can be found in several texts such as Skoog and West (1980) and Willard and others (1981) or in manufacturers' brochures.

Analytical procedures

Quantitative analysis by colorimetry is an extremely useful tool because it has wide applicability, high sensitivity, moderate- to-high selectivity, good accuracy, and is easy and convenient to use (Skoog and West, 1980). Additionally, many colorimetric procedures are readily automatable, which leads to significant increases in throughput rates.

Before analysis is conducted, a set of working conditions and (or) instrumental settings must be selected. The selection of a wavelength at which absorbance measurements are made is

of primary importance. The wavelength selected is commonly an absorbance peak, because changes in absorbance per unit of concentration are at a maximum. In this way, maximum sensitivity is obtained. This wavelength selection, in turn, provides several advantages in addition to extending the determination to the lower concentration ranges: the interferences from other ions are minimized, the effect of natural color and (or) turbidity is reduced and may become insignificant, small sample volumes can be used, measurements are made less sensitive to problems associated with a lack of monochromaticity, and Beer's law is adhered to in the analysis.

Once working conditions have been selected, analysis of samples can begin. In its simplest form, colorimetry or spectrophotometry entails the duplication of a color formed by the constituent of interest by some type of reagent or reagents. Thus, the color of some unknown sample solution becomes exactly the same as that of a solution containing a known concentration of the constituent being measured when both solutions have the same amount of colored substance in a fixed volume (when Beer's law is followed). In actual practice, such a procedure requires a great deal of time and effort and is generally impractical. Commonly, an analytical curve for the constituent being determined is constructed by plotting absorbance versus concentration for known solutions. The standards used to construct such a curve are selected such that they approximate the concentration range of the unknown samples that are being analyzed and generally cover a range in which Beer's law is obeyed. The standards are treated in exactly the same fashion as an unknown sample solution for the development of color and for the measurement of absorbance. Plots of absorbance versus concentration are made; then, by measurement of the absorbance of an unknown solution, constituent concentration can be determined by reference to the existing analytical curves. Such standard curves may be used repeatedly if identical analytical conditions are maintained; but, experience has shown that these curves must be checked frequently because identical conditions are rarely achieved even over short periods of time (for example daily).

Interferences

Several factors influence the absorbance of a material. These include the type of solvent, the temperature, the solution pH, high electrolyte levels, and the presence of interfering substances. The effects of these variables must be known and accounted for in establishing analytical conditions. Through proper selection and maintenance of constant conditions, many of these variables can be dealt with effectively so that precise and accurate results are produced simply by following the analytical procedure; however, some cases do require additional measures to produce good analyses. Typically, additional measures are needed because of the presence of interfering substances that can have either a positive effect (providing increased color leading to higher absorbance readings and hence, spuriously high results) or a negative effect (reducing the color causing lower absorbances and, hence, spuriously low results).

Interferences tend to be of two types, either physical or chemical. Physical effects encompass such things as natural color and turbidity, and almost always cause positive interferences. Chemical effects can cause either positive or negative interferences. An example of a positive chemical interference is the presence of a substance that reacts with a color reagent in the same way as does the constituent of interest. Thus, the resulting color represents not only the constituent, but also the foreign substance. An example of a negative interference is the presence of a substance that inhibits the formation of color by complexing the constituent of interest so that it cannot react with the color reagent.

The simplest way of dealing with interfering substances is to dilute them to the point of insignificance. This strategy works only if the sensitivity of the method is sufficient to determine the constituent of interest at low concentrations. Where dilution is not feasible, other means must be used either to remove the interfering substance, to increase the selectivity of the method, or to compensate for the effect of the interfering substance. Removal may be accomplished in a number of possible ways. However, because the selection of an appropriate procedure is dependent upon the sample

matrix and the constituent of interest, care must be exercised before adopting any procedure. If turbidity is the problem, sample filtration through a 0.45 μm membrane filter may eliminate it. Centrifugation is sometimes another satisfactory alternative. If color interferes, oxidation (using HNO_3, or H_2O_2) or bleaching may possibly eliminate it. Chemical interferences can sometimes be removed by using ion-exchange resins, solvent extraction, or precipitation.

There are several ways to improve method selectivity. Among such means are (1) adjusting the pH such that the constituent of interest complexes with the color reagent much more favorably than with interfering ions or (2) using masking compounds such as EDTA that form stable, unreactive complexes with interfering ions and, thus prevent their reaction with the color reagent. Compensation can be accomplished in several ways. Direct compensation can be made by adding all reagents except the color reagent to the sample, placing the sample in the spectrophotometer, setting the absorbance to zero, and then adding the color reagent and measuring the absorbance. This procedure eliminates the natural absorbance of the water, but it has limited utility (it can be used only when the absorbance curve has a shallow slope in the operating region). Another procedure entails subtraction of natural color absorbance. To do this, determine the absorbance of the test sample versus the blank sample specified for the method. Then determine the absorbance of the natural-color sample versus distilled water under the same spectrometric conditions used for the test sample. The difference between the two readings is the corrected absorbance and this value is used to obtain concentration. The natural-color sample is prepared by adding all reagents but the indicator (color) reagent to the same volume of sample water as used for the test sample. Instead of the color reagent, add an equal volume of indicator solvent (usually distilled water).

Automated analyses

The popularity of automated analyzers has increased greatly over the years because of their ability to analyze samples at a much faster rate than is possible using manual procedures. Additionally, for many substances automated analyzers can produce results that are more precise and accurate than those of manual procedures. Finally, most automated analyzers can be networked to mini-computers or mainframe computers, which facilitates sample handling, increases the speed and accuracy of data transfers, and often provides real-time quality control. Today, automated analyzers for colorimetry or spectrophotometry tend to fall into one of three categories: continuous segmented flow, discrete, or flow injection.

Continuous segmented flow systems, such as the Technicon Autoanalyzer, consist of a sampler, a proportioning pump, a cartridge (chemistry) manifold, a filter photometer, a recorder, and a printer. Solutions are introduced into the analytical system by the sampler. The sample solutions are poured into small cups or test tubes that are placed in a rotating turntable, which advances at preset times, and the samples are aspirated from each cup. A wash solution is aspirated for a timed interval between samples. The proportioning pump works on a peristaltic principle and meters samples, reagents, and air bubbles into the flow system through various sizes of flow-calibrated pump tubing. The cartridge manifold comprises the arrangement of reagent additions, mixing coils, delay coils, and a heating bath (if needed to make the reaction proceed at an acceptable rate). These components vary in complexity and detail for each determination. The colorimeter is usually a two-photocell filter photometer. The output from the colorimeter is measured on a recorder and, possibly, on a printer. An analytical curve can be constructed after a sufficient number of standards have been analyzed. Sample concentrations are then obtained from the curve. Alternatively, a printer can be used, that reads directly in concentration, but these values must also be adjusted by reference to an analytical curve.

Flow injection analyzers are continuous flow systems that utilize an unsegmented analytical stream; thus, they differ from continuous segmented flow systems because no air bubbles are involved. In construction, flow injection systems

are similar to segmented flow analyzers in that they require a sampler, a pump, a reaction manifold, a detector, and readout device. The differences involve the use of an injection valve and a microprocessor. The latter is necessary to control the timing of the system and to reduce the data. A sample is introduced into the system as a plug (or slug) through the use of an injection valve. This plug is then placed into a continuously flowing system that consists of a carrier (usually distilled water, but reagents may also be included). Mixing of samples and reagents occurs through diffusion processes. As a result, the reactions that produce color or turbidity rarely go to completion (do not achieve a steady state). Therefore, three critical factors must remain constant: (1) sample injection volumes, (2) pumping rates for the carrier and reagents, and (3) residence time in the analytical manifold and detector.

As samples are drawn into the system by an automatic sampler, a pump simultaneously moves the carrier into the sample stream. A sample fills the injection valve until it is loaded; the valve is then opened and the analytical stream is flushed out the valve, thus creating the requisite plug. This stream then moves into a reaction manifold where analytical processing (addition of reagents, heating, dialysis, ion exchange, etc.) takes place. The resulting solution is then passed through the flowthrough cell of an appropriate detector, as in a segmented system. As with segmented flow, an analytical curve must be established so that sample concentrations can be obtained. The absence of air segmentation leads to higher sample throughput and there is little or no carryover between samples.

Discrete analyzers, such as the American Monitor IQAS or the Coulter IKL, differ from both continuous segmented flow and flow injection systems in that they operate exposed to the atmosphere, rather than sealed in tubing and glass. Each reaction, which produces a colored or turbid product, takes place in a discrete (hence the name) container, which is usually disposable. In essence, these systems are "robot chemists," capable of performing a large variety of tests (as many as 32), using the same instrumentation. Requisite chemicals and diluents, for each test, are stored in the unit and dispensed as needed. These types of analyzers are operated by programmable mini-computers that control sampling, reagent type and volume, mixing, heating (if needed), incubation time, wavelength selection, color measurement, calculation of analytical curves, and determination of sample concentrations. These concentrations do not require additional correction because they are automatically calculated from an analytical curve. Data are provided in print and are also stored in the mini-computer for direct transfer to a mainframe system. Because discrete analyzers use open-reaction containers, certain types of analytical procedures either cannot be employed or require that samples undergo some type of pretreatment prior to insertion in the system. For example, the cadmium-reduction method for the determination of nitrate plus nitrite cannot be adapted to a discrete analyzer. Likewise, the methylthymol blue method for the determination of sulfate, which calls for the removal of divalent cations through the use of an ion-excange column, cannot be run directly as with a continuous flow system. However, if the samples undergo pretreatment to remove divalent cations, a discrete analyzer can be used to quantitate sulfate using this method.

References

Kolthoff, I. M., Sandell, E. M., Meehan, E. J., and Bruckenstein, S., 1969, Quantitative chemical analysis (4th ed.): London, The Macmillan Co., 1199 p.

Sandell, E. M., 1959, Colorimetric determination of traces of metals (3rd ed.): London, Interscience Publishers Ltd., 1032 p.

Skoog, D. A., and West, D. M., 1980, Principles of instrumental analysis (2nd ed.): Sanders/New York, Holt, Rinehart, and Winston Inc., 69 p.

Skoog, D. A., and West, D. M., 1982, Fundamentals of analytical chemistry (4th ed.): Saunders/New York, Holt, Rinehart, and Winston Inc., 603 p.

Willard, H. H., Merritt, L. L. Jr., Dean, J. A., and Settle, F., 1981, Instrumental methods of analysis (6th ed.): New York, D. Van Nostrand Co., 1030 p.

Electrometry

Voltammetry

Voltammetry, polarography, is based on current-voltage measurements at an electrode. When a potential is applied across an electrode pair, the working electrode becomes polarized by assuming the applied potential. The working electrode remains polarized, with no flow of current, until the potential difference between the electrodes is sufficient to exceed the decomposition potential of a particular electroactive analyte in solution. At potentials greater than the decomposition potential, the electroactive analyte is deposited on the working electrode and the current begins to flow. As the applied potential is increased further, the change in current levels, and becomes diffusion-limited.

The potential at which the current produced by the electrochemical reaction reaches one half its diffusion-controlled value is the half-wave potential, $E_{1/2}$. The half-wave potential is characteristic of the particular electroactive analyte undergoing reaction and may be used for identification purposes; however $E_{1/2}$ is a function of solution conditions such as the supporting electrolyte, the pH, and the solvent system, to name a few.

The current measured is the sum of the Faradiac, capacitative, and residual contributions. Faradiac current is a result of electron transfer across the electrode-solution interface as the result of the oxidation or reduction of the electroactive analyte at the working electrode. Faradiac current is proportional to the concentration of the analyte.

Capacitative current is the current needed to charge the double-layer capacitance at the surface of the working electrode. The separation of charge at the solution-electrode interface acts much like a large capacitor with respect to the external circuitry and requires current for charging. Capacitative current represents an inherent offset or noise and can be the principal limitation to sensitivity of a polarographic measurement. However, capacitative current can be minimized by modulating the applied potential and by maintaining a constant working electrode area.

The residual-current contribution to the total diffusion current can be evaluated by measuring the current resulting from the supporting electrolyte alone. The residual current at any particular potential can then be subtracted from the total current at that potential.

Polarography uses two basic forms for the working electrode—liquid or solid. The majority of polarographic techniques use various configurations of elemental mercury electrodes. Mercury electrodes generally take form either as a suspended mercury drop, known as the hanging mercury drop (HMD) electrode or as a dispersed thin-film electrode deposited on a conducting substrate, commonly referred to as the mercury thin-film (MTF) electrode. In general, greater sensitivity may be obtained on MTF electrodes, but HMD electrodes are simpler to use and more versatile. Solid electrodes include platinum, gold, and various forms of graphite. Major limitations of solid working electrodes are their variability in the activity of the deposited analyte and their inability to accommodate more than one simultaneously reduced analyte. Both limitations of solid electrodes prevent useful current-potential response when applied to stripping polarographic techniques.

Modern polarographic instrumentation employs a three-electrode system composed of a working electrode, an auxiliary electrode, and a reference electrode. The electrochemical reaction takes place at the working electrode, and the auxiliary electrode completes the circuit between the working electrode and the solution. The reference electrode serves as a contact to measure potentials applied to the working electrode. Platinum wires and foils are commonly used as auxiliary electrodes. Reference electrodes are usually either the familiar calomel reference electrode or the silver-silver chloride reference electrode.

A technique based on polarographic principles is anodic stripping voltammetry (ASV). ASV consists of two sequential steps. First the electroactive analytes are preconcentrated, or deposited, in the working electrode by reduction. After sufficiently long deposition times,

the concentration of the analyte will be greater in the electrode than in the sample solution. Secondly each analyte is subsequently stripped, or oxidized, from the working electrode. In ASV the deposition step occurs at a sufficiently negative potential as to deposit all the desired analyte species into the working electrode. During the stripping step the applied potential is stepped anodically under carefully controlled conditions, and the preconcentrated analytes are subsequently stripped completely into the bulk solution. Carefully controlled conditions are necessary to obtain precise current-potential responses for quantification and identification, respectively.

The total current generated by the electrochemical reaction during ASV is, again, the sum of the Faradiac, capacitative, and residual contributions. Differential pulse anodic stripping voltammetry (DPASV) minimizes the capacitative contribution by using a working electrode having a fixed electrode area and by superimposing a modulated pulse on the applied potential step. Two current measurements are made during each potential step. The first occurs just prior to the occurrence of the modulation pulse and the second, immediately following it. The change in current between the pair of measurements minimizes the capacitative current and therefore enhances the signal-to-noise ratio. The contribution due to the residual current can be eliminated by subtracting the reagent-blank voltammogram from the sample voltammogram.

Ion-selective electrodes

Ion-selective electrodes are electrochemical sensors that relate concentration to electrical potential. They operate in the same way, irrespective of type, as does the classical glass electrode for the measurement of pH. Each sensor consists of an internal electrode and a membrane that establish a potential. This potential is linearly dependent on the logarithm of the activity of a given ion in solution. Effective concentration ranges usually cover several orders of magnitude. This electrode response is called "Nernstian" and can be expressed mathematically as follows:

$$E = E_x + 2.3\ RT/nF \log A$$

E is the total potential, in millivolts (mv), developed between the selective ion and the reference electrodes; E_x, in mv, varies with the choice of reference electrode; 2.3 RT/nF is the Nernst factor, where R is the gas constant, F is the Faraday constant, n is the charge on the ion, including the sign, T is the temperature in degrees Kelvin; and A is the activity of the ion to which the electrode is responding. The term 2.3 RT/nF is equal (at T=25 °C) to 59.16 mv when n=1, 29.58 mv when n=2, etc.

As noted in the above equation, the electrochemical potential determined under real conditions is a measure of the activity of the ion in question. This relates concentration to the interaction of the specific ion with all other ions in solution. The activity-concentration relationship A can be described by the following equation:

$$A = cf$$

where c is the concentration of the ion determined and f is the activity coefficient. The magnitude of the interaction depends on the total ionic strength of the solution. This can be maintained at a constant level by the addition of a high concentration of an inert electrolyte to the system. Properly chosen, this addition would not affect the equilibrium of the ion being measured and would stabilize the activity coefficient. Therefore, to determine concentration, one needs only to provide the means for measuring with a readout device of some type this electrochemical potential with respect to a constant reference potential. By relating the potential measured by such a system to a series of known standard solutions, one can calibrate, and, subsequently, determine the concentration of the ion in an "unknown" sample. Additional information on the theory of ion-selective electrodes and instrumentation may be found in the manufacturers' literature; in Marenthal and Taylor, 1973; in Andelman, 1971; in Moody and Thomas, 1971; and in Durst, 1969.

For the purpose of discussion, ion-selective electrodes can conveniently be grouped into three general types: solid state, liquid membrane, and gas sensing. Each one finds use in water-quality applications.

Solid-state, ion-selective electrodes are normally constructed by sealing a crystal membrane in an epoxy tube or other appropriate holder. Two types are available, either homogeneous or heterogeneous crystalline electrodes. The homogeneous membrane electrode consists of an appropriate crystalline material prepared from either a single compound or from a homogeneous mixture of compounds having satisfactory electrical resistance. The principal advantages of homogeneous electrodes are their low cost, fast response, long operative life, resistance to corrosive acid and alkaline media, and Nernstian behavior throughout many decades of use. Electrodes of this type have been developed with high selectivity for bromide, chloride, fluoride, iodide, silver, and sulfide.

The fluoride ion-selective electrode consists of a single crystal of lanthanum fluoride (LaF_3) membrane bonded into an epoxy body. A solution containing fluoride ions and a silver wire, which provides electrical contact to the back of the crystal, are sealed inside. The crystal is an ionic conductor in which only fluoride ions are mobile. When the electrode is placed in an external solution containing fluoride, fluoride ions migrate across the membrane in an attempt to reach a state of equilibrium. A stable potential is developed that is measured.

The heterogeneous electrode consists of an active substance or a mixture of active substances mixed with an inert matrix, such as silicone rubber or polyvinyl chloride, or placed on hydrophobized graphite, to form a sensing membrane that is heterogeneous in nature. An example of this type of solid-state electrode is silver iodide embedded into silicone rubber to provide iodide ion-selective response.

The second type of electrodes, liquid-membrane sensors, is similar to the solid-state electrodes. Instead of a crystal-type membrane, these electrodes use a liquid ion exchanger tailored as a specific carrier for the ion of interest. The ion exchanger is held in place by a thin, porous, inert membrane. There is no shortage of prospective liquid cation- and anion-exchanger materials for possible use in ion-selective electrodes; however, the successful fabrication of these electrodes presents problems, many of which are mechanical. The liquid ion exchanger must be in electrolytic contact with the sample, but any mixing of phases must be minimal; must not be too soluble in the sample solution, which will effect the limit of detection; must have a viscosity high enough to prevent its rapid loss by flow across the membrane; must possess good stability; and must be available in a state of high purity with high-exchanger capacity. The liquid ion exchangers are usually high-molecular-weight organic compounds dissolved in an organic solvent. The organic molecule has charged sites where the ion of interest can bind to it. Both the exchanger and the ion of interest move through the membrane. An internal filling solution and a silver wire coated with silver chloride provide the electrical contact. As with the solid-state electrode, a stable potential is developed and measured. A calcium selective-ion electrode as described by Willard and others, 1974, is a good example. An organic derivative of phosphoric acid is used as the liquid ion exchanger that selectively forms a strong salt with calcium. Liquid-membrane electrodes selective for potassium, nitrate, and fluoroborate, to name a few, are also available.

The most recent type of membrane introduced, which is useful in water analysis, is the gas-sensing electrode. In addition to being used for measuring dissolved gases in solution, they can be used for measuring the ionic form of a constituent after appropriate sample treatment to convert the ion to a gas. The sensor, composed of an indicating and a reference electrode, uses a gas-permeable membrane to separate the sample solution from a thin film of an intermediate solution, which is either held between the gas membrane and the ion-sensing membrane of the electrode or is placed on the surface of the electrode using a wetting agent (for example, in air-gap electrodes). This intermediate solution interacts with the gaseous species in such a way as to produce a change in a measured value (e.g., pH) of the intermediate solution. This change is then sensed by the ion-selective electrode and is proportional to the partial pressure of the gaseous species in the sample. An example is the ammonia-sensing electrode, which uses a hydrophobic gas-permeable membrane to separate the sample solution from the electrode-internal solution. Dissolved ammonia in the sample diffuses through the membrane in proportion to its concentration,

and, in turn, reacts in the internal solution to produce hydroxide ions. This changes the pH of the internal solution. This change is measured by a pH electrode located behind the membrane. Because the pH varies directly with the ammonia concentration, the electrode responds directly to ammonia.

Similar schemes can be devised for other gases, including nitrogen oxides (NO_x), carbon dioxide (CO_2), hydrogen sulfide (H_2S), and hydrogen cyanide (HCN). The ion-selective electrode does not have to be a pH electrode as in the case for ammonia; the choice is dependent upon the reaction of the gas in the internal solution.

A reference electrode is required to complete the measuring circuit by providing a conductive path from the sensing electrode, through the solution, to the readout device. The reference electrode is the half of the electrode pair that provides a constant potential regardless of solution composition. The potential developed by the sensing electrode is measured with respect to this reference potential to give an overall system potential, which can be converted to the level of the species sensed. Numerous types of reference electrodes are available. The analyst should consult the manufacturer's manual for the reference electrode that should be used for a specific selective-ion electrode. Differences in performance among the various forms of reference electrodes can be a major factor in optimizing a method of potentiometric analysis.

Instrumentation required for potentiometric analysis with ion-selective electrodes is relatively simple and inexpensive. Measurements can be made with conventional pH meters that provide scale expansion. This type of instrument displays voltages, pH units, or other concentration units by means of a needle pointer and scale. Modern, direct-reading, solid-state potentiometers are ideally suited for the requirements of water analysis. This type of meter provides digital display in millivolt or pH units. Operator error is reduced with digital instruments, because there is no need for interpolation and no risk of confusing scales. Instruments are available under the designation of "Selective Ion-Meter," which measure the potential of pH- and ion-selective electrodes and display it directly in concentration or activity units on a logarithmic scale. Millivolt scales are also provided for titrations and to verify proper electrode operation.

An electrode interference is any species, other than the ion being measured, in a sample solution that can alter the potential measured by a sensing electrode. Two types of interferences exist: "electrode" and "method." Electrode interferences are those substances that give a response similar to that of the ion being measured and whose presence generally results in an apparent increase in activity or concentration of the ion being determined—those substances that interact with the membrane so as to change its chemical composition; and electrolytes present at a high concentration that produce appreciable liquid-junction potentials. Method interferences are substances that interact with the ion being measured so as to decrease its activity or apparent concentration, although the electrode continues to report the true activity.

Generally, interferences for solid-state electrodes (except for fluoride) are species that form more insoluble salts or metal sulfides than does the ion of interest. Liquid-membrane electrodes react to the interfering ion as though it were the ion of interest. Gas-sensing electrodes are affected by any species that has a finite vapor pressure under the measuring conditions of the gas of interest. For a discussion of interferences for a particular species, see the individual constituent of interest in this chapter.

Specific conductance

Specific conductance is determined by using a Wheatstone bridge, in which a variable resistance is adjusted so that it is equal to the resistance of an unknown solution between two electrodes either of platinized platinum or of other suitable material such as graphite. The null point is detected by an alternating current galvanometer, cathode-ray tube or digital readout. Alternating current is necessary to prevent polarization of the electrodes. Direct current produces gas bubbles on the electrodes that greatly increase the resistance and change the concentration of the electrolyte in the vicinity of the electrodes. The electrodes are coated with a thin layer of amorphous platinum, which

tends to absorb gases and catalyzes their reunion, thereby minimizing polarization.

The electrode cell may be the dip, cup, or pipet type. The pipet cells are generally preferred for routine laboratory use: because they require a smaller volume of water for the determination, the water can be drawn directly from a narrow-mouth sample bottle without transferring it to another container, the total time for the determination is less, and the water sample undergoes less mechanical agitation. Dip- or cup-type cells are preferable for field work.

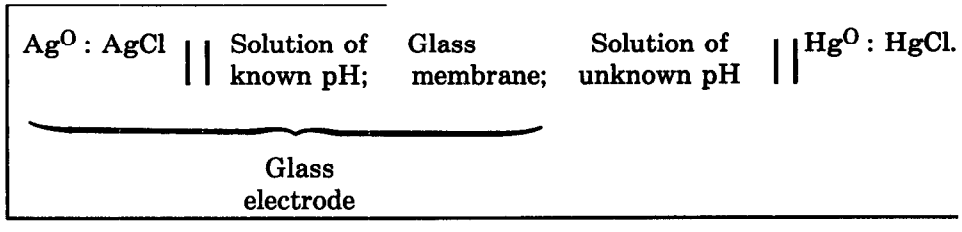
Temperature is an important factor in determining the specific conductance of a solution. When the temperature of a solution increases, the conductance almost always increases. By convention, 25 °C is the standard reference temperature in most water-resources applications. Thus, all specific-conductance determinations are adjusted to and specified at 25 °C. The adjustment to 25 °C is achieved either automatically with a thermistor within the sensor or manually at the conductivity bridge. Automatic or manual temperature compensation is proportional to the inverse of the resistance of a standard potassium chloride solution.

Many direct-reading conductivity bridges are commercially available that are well suited for both laboratory and field work. Manufacturers, such as Beckman, Lab-line, YSI, etc., produce lines of durable, lightweight equipment. These direct-reading conductivity instruments have either a dial for manual temperature compensation or automatic temperature compensation built into the conductivity cell and bridge circuit. As with all instruments, the manufacturers' instructions and supplemental instructions should be followed exactly for good precision and accuracy.

pH

pH meters measure the electrical potential between two electrodes immersed in the solution to be tested. The reference electrode maintains a constant potential, and the indicating electrode maintains a potential dependent on the hydrogen-ion activity of the solution. The calomel electrode, which is a widely used reference electrode in water analysis, consists of a mercury-calomel rod immersed in a saturated solution of potassium chloride. This electrode has a half-cell potential of +0.246 volt. Electrical connection with the sample is provided through porous fibers sealed into the immersion end. A hydrogen-ion-selective glass electrode is normally used as an indicating electrode. The glass electrode has several features that recommend it for pH measurements. Among the most important are that it is not affected by oxidizing or reducing substances in the sample and that it can be used to measure the pH of turbid samples or colloidal suspensions or both. The basic design is a silver-silver chloride or mercury-mercurous chloride electrode immersed in a solution of known pH and completely sealed in glass.

The mechanism by which the glass membrane responds to hydrogen-ion activity involves absorption of hydrogen ions on both sides of the membrane proportional to the activity of the hydrogen ions in solution. The cell for measuring the pH of a solution is of the following type:



The half-cell potential of the glass electrode is a logarithmic function of the difference in hydrogen-ion activity of the solutions on either side of the glass membrane. To measure this potential a high-impedance electrometer circuit is used, because the resistance of the glass membrane is so great.

Desired features in a line-operated pH meter are a built-in voltage regulator; an accuracy of at least 0.02 pH; stability of calibration; a

built-in temperature-compensating mechanism; durable electrodes; and a design that permits insertion of the electrodes, a stirrer, and a buret into a suitable vessel for titrations. For pH determinations in the field, the instrument should also be rugged, compact, and battery operated. pH meters should be carefully calibrated with two buffer solutions that bracket the pH range of the test samples, and the calibration should be checked during extended periods of operation. A third standard buffer should be used—the data of this third buffer will automatically indicate stressed or faulty electrodes if the theoretical versus actual curve is non-linear.

References

Andelman, J. B., 1971, Analysis for metal pollutants: Instrumental Analysis for Water Pollution Control, Michigan, Ann Arbor Science, p. 241–3.

Bates, R. G., 1978, Concept and determination of pH: In Treatise on Analytical Chemistry, New York, Wiley-Interscience, part 1, v. 1, p. 821.

Durst, R. A., ed., 1969, Ion-selective electrodes: National Bureau of Standards Special Publication 314, U.S. Government Printing Office, Washington, D.C., 452 p.

Maienthal, E. J., and Taylor, J. K., 1973, Electrochemical techniques in water analysis: Water and Water Pollution Handbook, New York, Marcel Dekker, Inc., v. 4, p. 1751-97.

Moody, G. J., and Thomas, J. D. R., 1971, Selective ion sensitive electrodes: England, Merrow Publishing Co. Ltd., 140 p.

Ion chromatography

Principles

Ion chromatography (IC) has been used since the early 1940's for separation of both organic and inorganic species. Analysis was relatively easy when the ion being eluted from an ion-exchange column had a directly measurable property, such as absorption in the ultraviolet or visible region of the spectrum, that could be distinguished from the background. Specific-conductance measurements were also used, but high-background conductance of the electrolyte (eluent) usually overwhelmed the conductance of eluting ions. Small and others (1975) solved this detection problem by adding a suppressor column downstream from the separator column that suppressed or neutralized ions of the background electrolyte. Recent advances in cells and electronic suppression have revived the original technique. However, methodology in this manual uses the technique of Small and others (1975), and discussion is limited to the two-column technique.

A sample is injected into a liquid mobile phase being pumped through two ion-exchange columns placed in series. In the first column, called the separator, ions are separated on the basis of their affinity for exchange sites on the resin. The second column, called the suppressor, decreases the background conductivity of the mobile phase, called the eluent, to a minimal level and pairs the ions in the sample to some highly conductive species. Separated ions are quantitated with a specific-conductance cell. The basic procedure for anions, such as fluoride, is shown in figure 5. A typical chromatogram for seven of the common anions found in water is shown in figure 6.

IC is most useful for the determination of the major ionic constituents of aqueous samples in which no single ion is in great excess of the other ions. The ions are determined sequentially using only a small aliquot of sample, and detection limits for many of the ions are lower when IC is used instead of other techniques. Chromatographic separation of the ions eliminates many of the interferences associated with other techniques, permits the use of universal detectors, and is capable of determining different species of the same ion in some cases.

Apparatus

The IC technique and equipment are rapidly changing and improving. Better pumps, sample

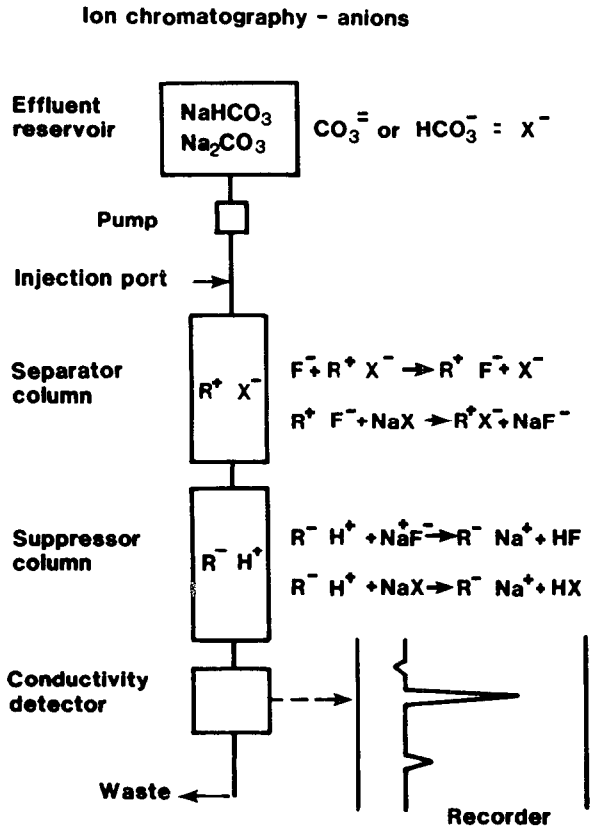


Figure 5.—Ion chromatography system for anions

injection systems, separator resins, suppression techniques, and a proliferation of detectors promise greater accuracy, precision, and versatility.

Pumps

Liquid chromatography requires a highly reproducible eluent flow rate for reproducible results. For this reason, intermittent-displacement-type pumps are used in IC instruments. Recent advances in pump technology have resulted in a new generation of intermittent-displacement-type pumps for IC use. They have pump heads made entirely of nonmetallic parts and can operate at pressures as high as 2,000 pounds per square inch. These pumps also incorporate a precision pressure transducer in dual-pressure and flow-rate feedback loops to provide a constant-pressure, essentially pulseless, eluent flow.

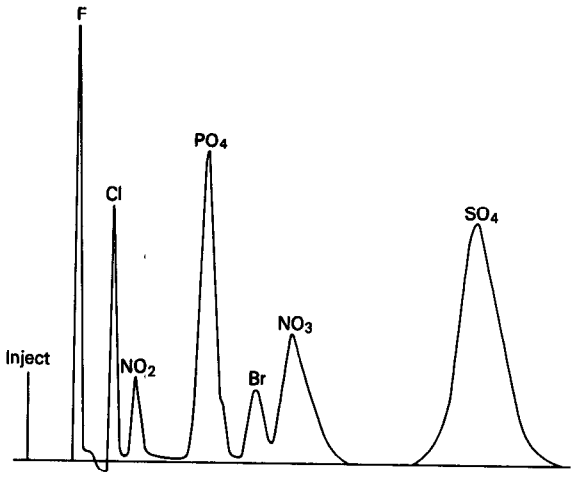


Figure 6.—A typical chromatogram for seven anions

Determining low concentrations of ions in precipitation samples requires that the conductivity meter on the ion chromatograph be set to more sensitive scales. Hence the "water and carbonate dip" interference with fluoride and chloride determinations at low concentrations is more pronounced. To eliminate the "water and carbonate dip," a stronger eluent is added to each sample to increase the conductivity to the same level as that of the eluent that flows through the system. This modification of the ion chromatograph can be made by installing two pulseless pumps, which permit the automatic addition of stronger eluent to each sample. The ion chromatographic schematic in figure 7 includes this automatic addition.

Sample-injection systems

Reproducible sample injection can be very difficult to achieve in IC. One problem is that the ions amenable to determination are ubiquitous in the laboratory environment, presenting substantial opportunities for sample contamination. Especially problematic is the determination of ions at low levels in samples such as precipitation or boiler feed water.

The most common sample-injection technique for IC is to manually rinse and fill a sample loop from a plastic syringe, and then place the loop into the chromatographic system, causing the

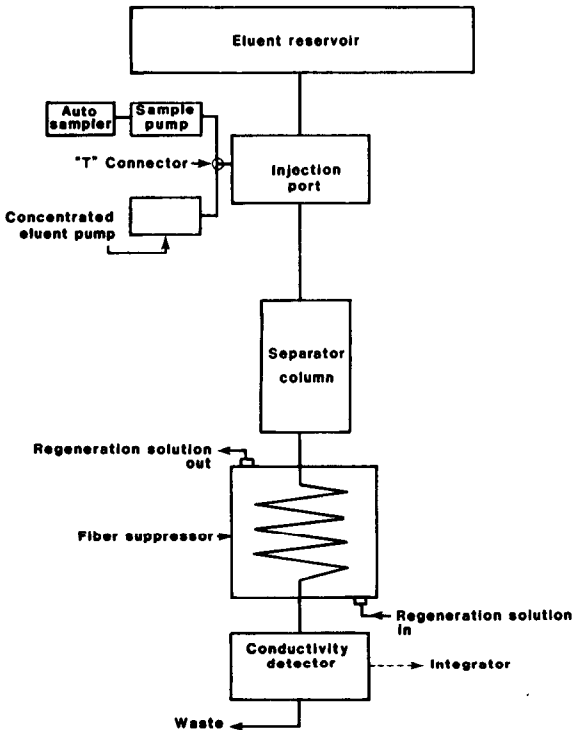


Figure 7.—Ion chromatographic schematic diagram

sample to be swept onto the separator column by the eluent flow.

Automated instruments may use a pump to fill the sample loop. This pump should always be on the waste side of the sample loop to prevent contamination from the pump mechanism. Another approach is to use an automatically actuated valve to open a vacuum line and draw the sample through the sample loop. In any case, some means must be incorporated in the injection- system design to divert eluent flow while the sample loop is being filled or moved in and out of the chromatographic system. Otherwise, a pressure spike will upset the system upon sample injection.

Separator resins

The most commonly used separator resins are S-DVB (styrenedivinylbenzene) based. These are pellicular resins, which have exchange sites only at or very near the surface of the S-DVB support. This leads to high efficiency by minimizing the diffusional pathways of the sample ions and results in good mass-transfer characteristics for the resin.

The stability of these resins throughout the entire pH range is their most important feature. S-DVB packings do not undergo degradation even under drastic conditions. Swelling in organic solvents is minimal. Ion selectivities on these resins are similar to those for conventional S-DVB packings. They are resistant to overloading and poisoning.

Depending on the analyte, two types of S-DVB-separator packings are used. Cation separators use surface-sulfonated S-DVB resin and have typical capacities in the range of 0.005 to 0.1 me/g. Anion-separator resins have an inert, hydrophobic, S-DVB-polymer core. Surrounding this core is a layer of solvated sulfonic acid groups similar to that used in cation separators. This layer is coated with a uniform monolayer of laminated latex. The latex is attached to the sulfonated surface by a combination of electrostatic and Van der Waals forces. The capacity of these anion-exchange resins is similar to the capacity of the cation exchangers.

Pellicular silica-based packings, which have functional ion-exchange groups attached by the usual silane reactions, are of some use in IC, as well as resins such as silica-coated polyamide crown resins (Igawa and others, 1981), dynamically coated reverse phases (Cassidy and Elchuk, 1982), and specially treated polymeric adsorbents of high-surface pourous polymers (Gjerde and Fritz, 1981). These techniques are in their infancy, having the pH limitations of silica, the liability of the silyl-carbon bond, or mechanical instability under the conditions necessary for good ion separations.

Suppressor resins

The original suppressors, still widely used, are columns packed with Dowex 1X8, 200–400 mesh in the hydroxide form for cation analysis and Dowex 50W X8, 200–400 mesh in the hydrogen form for anion analysis. These columns convert eluent ions to a low-conductivity species and paired analyte ions to highly conductive hydronium or hydroxide ions. These two processes, collectively called suppression, enable for very sensitive conductivity detection of ionic analytes.

This type of suppression system has two major drawbacks. The suppressor resin is slowly exchanged during a series of analyses and must be regenerated to the hydrogen or hydroxide form periodically. Regenerating the suppressor resin is time consuming and requires an entire IC-instrument subsystem consisting of a regenerant reservoir, a regenerant liquid pump, valving, and plumbing. The other major drawback is the increase in system volume that results from the suppressor column. Although having as large a suppressor as possible is desirable to avoid frequent regeneration, the larger the suppressor bed, the greater the peak broadening and general loss of chromatographic resolution.

Recently, Stevens and others (1981) introduced a hollow-fiber ion-exchange suppressor as shown in figure 8. It shows the reactions that occur across the membrane wall. Sodium bicarbonate/sodium carbonate eluent flows through the interior of the fiber and sulfuric acid regeneration solution flows countercurrently. The fiber is a cation exchanger containing sulfonate ($R\text{-}SO_3^{-1}$) exchange sites. When an eluent is flowing through the fiber, the cationic Na^{+1} ions are attracted to the SO_3^{-1} groups in the membrane wall, as are the protons present in the regenerant solution. The fiber-suppressor reactions are as follows:

Inside a tubular cation-exchange membrane:

$$2\ Na^{+1} + CO_3^{-2} + 2(\text{resin } H^{+1}) \rightarrow H_2CO_3 + 2(\text{resin } Na^{+1})$$

$$Na^{+1} + HCO_3^{-1} + \text{resin } H^{+1} \rightarrow \text{resin } Na^{+1} + H_2CO_3$$

$$\text{Resin } H^{+1} + NaF \rightarrow \text{resin } Na^{+1} + H^{+1}F^{-1}$$

Outside a tubular cation-exchange membrane:

$$H_2SO_4 \rightarrow 2H^{+1} + SO_4^{-2}$$

$$2Na^{+1} + SO_4^{-2} \rightarrow Na_2SO_4 \text{ (to waste)}$$

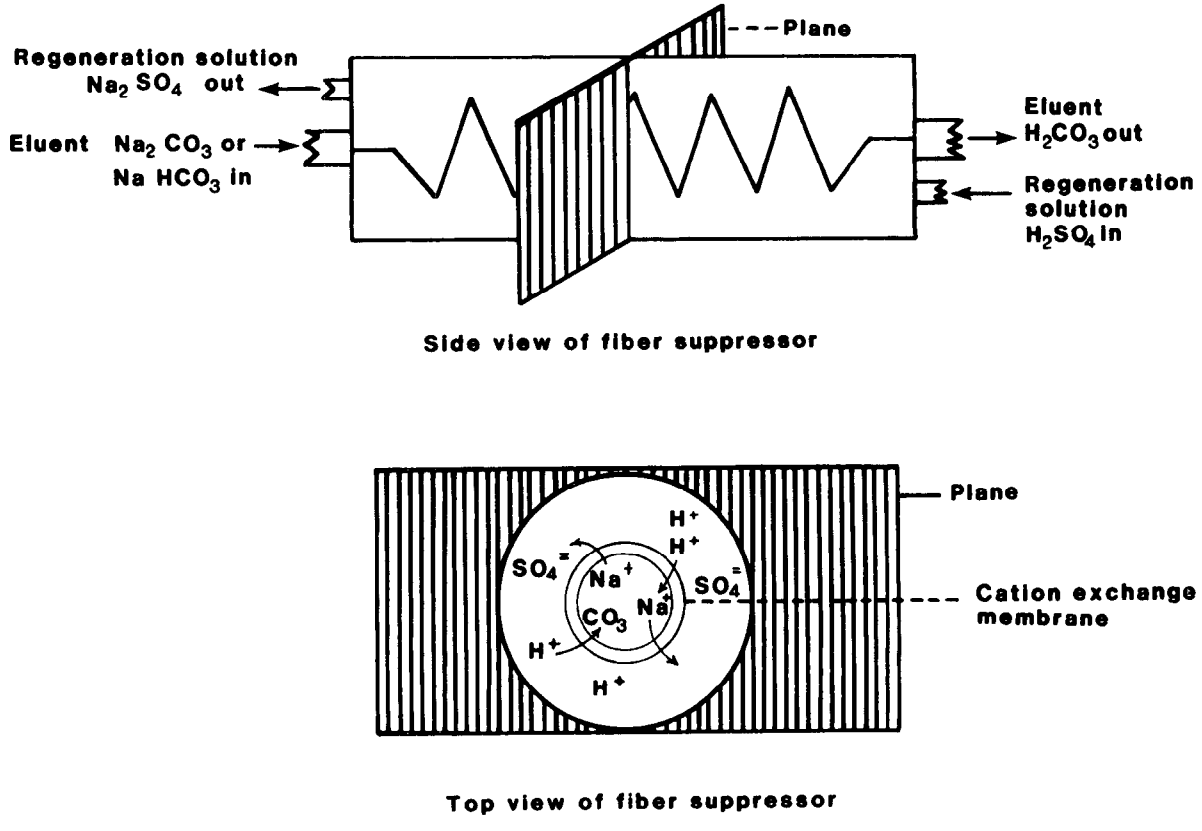


Figure 8.—Fiber suppressor

This device enables the near steady-state exchange of ions across the wall of a sulfonated polyethylene hollow fiber, resulting in the suppression of eluent and analyte ions.

The hollow-fiber suppressor eliminates the need for periodic suppressor regeneration, but results in greater band spreading and subsequent loss of resolution than is obtained using a small bed-volume, resin-filled suppressor column. Stevens and others (1982) reported that band spreading is reduced and resolution improved when the hollow fiber is surrounded with inert beads. Although some problems still need resolution, the steady-state suppressor device should improve greatly the utility of IC for accurate and precise quantitation. Upon entering a fiber suppressor, the eluting base, for example, NaOH, is removed by the acid resin:

$$\text{Resin } H^{+1} + Na^{+1}OH^{-1} \rightarrow \text{resin } Na^{+1} + H_2O$$

and the analyte anions (A^-) are converted to their acids:

$$\text{Resin } H^{+1} + M^{+1}A^{-1} \rightarrow \text{resin } M^{+1} + H^{+1}A^{-1}$$

which pass through the fiber suppressor and into a flow-through conductivity cell where they are detected.

Detectors

Small and others (1975) stated that it would be desirable to employ some form of conductimetric detection as a means of monitoring ionic species in a column effluent, because conductivity is a universal property of ionic species in solution and because conductance shows a simple dependence on species concentration. However, with older types of conductivity detectors the species of interest was generally "swamped out" by the more abundant eluting electrolyte. With the addition of the suppressor column, this problem was solved as discussed previously. Again, note that modern conductivity detectors have been refined to electronically suppress the eluting electrolyte. This will not be discussed further since the methods in this chapter utilize chemical suppression.

One problem with using conductivity for detection is its dependence on temperature. For each 1 °C change in temperature, there is a corresponding change of about 2 percent in the equivalent conductance. This temperature dependence severely limits analytical reproducibility if precautions are not taken to ensure temperature stability during IC analyses. Instruments, which are presently produced, incorporate a microprocessor-controlled conductivity detector that allows precise, accurate compensation for environmental-temperature fluctuations. This imparts both long- and short-term baseline stability and improved signal-to-noise ratios.

Conductivity is not the only means of detection compatable with IC. Electrochemical detectors are also commercially available. This type of detector works best in a high-conductivity background environment so no eluent suppression is required. The detector consists of a flow cell with three electrodes: a silver-silver chloride reference electrode, a platinum or steel counter electrode, and a silver or platinum working electrode.

The silver working electrode can be used to determine species such as cyanide, sulfide, and bromide. Setting the operating potential properly enables the detection of small amounts of bromide, for instance, in the presence of chloride concentrations high enough to swamp the bromide signal from a conductivity detector (Pyen and Erdmann, 1983). Unfortunately, reactions at the silver working electrode involve the catalytic oxidation of the silver electrode itself. For this reason variations in detector response within relatively short periods of time must be expected and frequent cleaning of the electrode surface is required. Suppression is unncecessary and toxic analytes, such as cyanide, remain in basic solution throughout the analysis (Bond and others, 1982).

Recently, post-column-reaction technology has been developed to produce complexes with the analyte ions that absorb in the near ultraviolet and visible portions of the spectrum. Detection is achieved using a photometer equipped with a flow-through cell. Some transition metals and different species of the same metal ion have been determined by this technique. One of the interesting applications involves the use of eluents

such as tartaric acid. This weakly acidic eluent permits the use of high-efficiency, silica-based separator resins. The resulting metal-tartrate complexes are monitored photometrically as they elute off the separator column.

An endless variety of detector types and configurations seem to be available. This instrumentation is perhaps where real progress in IC methodology will come in the near future.

Automation

Either peak height or peak area can be used to quantitate IC analyses with conductimetric detection. Measuring the peak heights or peak areas of both samples and standards can be tedious and time consuming because large amounts of data are generated in analyzing a sample. The use of an electronic integrator capable of reporting and storing both peak heights and areas facilitates the process. Hedley and Fishman (1981) described an automated system that was used for the determination of six anions in precipitation samples. The ion chromatograph was interconnected to an autosampler and a computing integrator. Slaina and others (1979) also described a data-acquisition and reduction system using a minicomputer. Presently, commercially automated instrumentation is available.

References

Bond, A. M., Heritage, I. D., and Wallace, G. G., 1982, Simultaneous determination of free sulfide and cyanide by ion chromatography with electrochemical detection: Analytical Chemistry, v. 54, p. 582–5.

Cassidy, R. M., and Elchuk, S., 1982, Dynamically coated columns for the separation of metal ions and anions by ion chromatography: Analytical Chemistry, v. 54, p. 1558–63.

Gjerde, D. T., and Fritz, J. S., 1981, Sodium and potassium benzoate and benzoic acid as eluents for ion chromatography: Analytical Chemistry, v. 53, p. 2324–7.

Hedley, A. G., and Fishman, M. J., 1981, Automation of an ion chromatograph for precipitation analysis with computerized data reduction: U.S. Geological Survey Water-Resources Investigations 81–78, 33 p.

Igawa, M., Saito, K., Tsukamoto, J., and Tanaka, M., 1981, Ion chromatographic separation of anions on silica-coated polyamide crown resin: Analytical Chemistry, v. 53, p. 1942–4.

Pyen, G. S., and Erdmann, D. E., 1983, Automated determination of bromide in waters by ion chromatography with an amperometric detector: Analytica Chimica Acta, v. 149, p. 355–8.

Slanina, J., Lingerak, W. A., Ordelman, J. E., Borst, P., and Bakker, F. P., 1979, Automation of the ion chromatograph and adaption for rainwater analysis: Ann Arbor, Michigan, Ann Arbor Science, Ion Chromatographic Analysis of Environmental Pollutants, v. 2, p. 305–17.

Small, H., Stevens, T. S., and Bauman, W. C., 1975, Novel ion exchange chromatographic method using conductimetric detection: Analytical Chemistry, v. 47, p. 1801–9.

Stevens, T. S., Davis, J. C., and Small, H., 1981, Hollow fiber ion-exchange suppressor for ion chromatography: Analytical Chemistry, v. 53, p. 1488–92.

Stevens, T. S., Jewett, G. L., and Bredeweg, R. A., 1982, Packed hollow fiber suppressor for ion chromatography: Analytical Chemistry, v. 54, p. 1206–8.