CHAPTER 20

EMISSION SPECTROSCOPY

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INTRODUCTION

Emission spectroscopy is that method of analysis that depends on the fact that energized atoms, ions, and molecules emit electromagnetic radiation when they lose energy. The characteristic line spectra emitted in flames, arcs, sparks, and related sources are highly specific for each element. Further, spectral line intensities are functionally related to element concentrations in the excitation source. Thus, when samples are introduced to these sources, both qualitative and quantitative analyses can be accomplished.

As a survey method, probably no other analytical technique provides so much information for a given amount of effort. A wide variety of sample types and forms can be analyzed, usually with a minimal amount of pretreatment. Up to 70 elements may be detected and estimated simultaneously, although procedures of this breadth are not generally attempted. The detection capability varies widely with elements, but it is generally best for the lower atomic number elements. Absolute detection limits are often below 10 nanograms which makes the technique quite useful for the analysis of small samples; i.e., one milligram or less. When sample size is not limiting, large spectrographs with high resolution readily provide detection capabilities as low as a few parts per million; and, in ideal cases, the limits may be as low as a few parts per billion.

In view of the above, it is not surprising that some of the earliest applications of emission spectroscopy were in the field of occupational health. Industrial workers are exposed to many substances containing toxic elements. Some elements tend to accumulate in body tissues and, therefore, very low concentrations of these elements in drinking water and/or air can be hazardous. For the safety of workers, it is necessary to monitor concentrations of toxic elements in the working environment and in body samples such as blood, urine and feces. The enormity of this analytical problem requires techniques of broad scope, high selectivity and detection capability, and adequate precision and accuracy. Emission spectroscopy is such a technique.

PRINCIPLES

Atomic line spectra are produced when energy is added to atoms in the ground state in an amount sufficient to cause some electrons to move from their normal energy levels to higher energy levels. In this form, the atom is said to be "excited." When the electrons return to their normal energy levels, they release energy stepwise in the form of radiation. Each step accounts for a definite amount of energy. The radiation produced has specific frequencies corresponding to the energies associated with the various steps, as indicated by the relationship $E = h\nu$.

where: E = energy of the radiation (photon)
h = Planck's constant
ν = frequency of radiation

An element is characterized by as many different spectra as the atom has electrons. Lines originating from the electron transitions of the neutral atom are called arc lines, whereas those from the singly ionized atom are called the first spark spectra. Although greater degrees of ionization do occur to a limited extent in conventional spectroscopic sources, the lines originating from neutral atoms and singly ionized atoms are the ones of major analytical interest.

The number of spectral lines produced for any element depends on the atomic structure. Elements with comparatively few valence electrons produce relatively simple spectra (e.g., alkalis and alkaline earth metals). In contrast, an element such as uranium produces thousands of discrete lines, none of which are very intense. The spectrographic determination of elements with very complex spectra is less attractive than for elements with simple spectra. This is due to possible incomplete resolution of lines of very similar wavelengths and also because elements with very complex, less intense spectra exhibit only fair detection limits.

While all the elements can be excited, gaseous elements, bromine and iodine are only infrequently determined this way. These elements can occasionally be determined with conventional excitation procedures by measuring the band spectrum of a compound such as calcium fluoride. However, this approach is not widely used. Carbon, phosphorus, and sulfur have their most sensitive lines below 2000Å and, therefore, require the availability of a vacuum spectrograph to overcome air absorption. Fortunately, most elements that are readily studied by optical emission spectroscopy produce useful lines between 2000 and 8000Å. In this wavelength region, simple optical, photographic and electronic equipment can be used to isolate and record spectral lines.

Qualitative analysis by emission spectroscopy is based on the fact that the atomic structure for each element is different. Therefore, a unique set of spectral lines is produced for each element; and these lines serve as a fingerprint. Line identification is usually accomplished by comparison of lines in the unknown spectrum with lines in a series of standard spectra prepared from pure elements.

Quantitative analysis is based on the fact that the intensity of a spectral line depends on the amount of parent element present in the excitation source. When the spectra are photographically recorded, relative intensities are estimated by measuring the optical density with a densitometer. Density values are then converted to relative intensities by means of an emulsion calibration curve relating these two variables for the particular emulsion involved, at the wavelength of interest. Alternately, line intensity can be recorded photoelectrically, thereby eliminating many of the errors inherent in photographic procedures.

SYSTEM COMPONENTS

Analysis by optical emission spectroscopy involves four main steps: 1) vaporization and excitation, 2) resolution of emitted radiation into constituent wavelengths, 3) recording spectral lines, and 4) interpretation.

Vaporization and Excitation

The total radiation output of a spectroscopic source is dependent on the aggregate of the processes of volatilization and excitation. Often, a clear distinction between these two processes is not made, probably because both are occurring simultaneously in most sources. For optimum reproducibility in the production of spectra, it is important to know which process is most important in a particular situation so that it may be properly controlled. The comprehensive treatise by Boumans[1] is an excellent source of information on this topic.

Vaporization can be accomplished by thermal means as exemplified by flames, direct current arcs, ohmic heating and laser evaporation. The commonly used high voltage spark discharge promotes vaporization by bombardment with positive ions and high velocity electrons. Of course, the vaporization process is seldom entirely thermal or entirely bombardment; and, therefore, no sharp separation between these sources should be assumed.

Flames. When a solution is aspirated into a flame in the form of minute droplets, desolvation occurs leaving small residue particles. Decomposition and vaporization of these particles produce a vapor containing atoms and molecules which are then excited via inelastic collisions with high velocity molecules liberated by chemical reaction between the fuel gases. Since the energy available in a flame is relatively limited, the spectra obtained are quite simple. As a consequence, spectral interferences are uncommon, thereby making it possible to employ comparatively inexpensive spectrometers of low dispersion.

Because of the comparatively low temperature of common flames such as air-acetylene, this source was traditionally considered suitable only for the determination of easily vaporized and excited elements such as the alkalis and alkaline earths. However, Fassel et al.[2,3] showed that many elements that tend to form stable oxides in normal stoichiometric flames can be dissociated to produce analytically useful atomic populations in a fuel rich oxygen-acetylene flame. Pickett and Koirtyohann[4] reported the successful use of the nitrous oxide-acetylene flame for the emission determination of many elements previously considered to be too refractory for analysis by this method. The development of a system for studying desolvation and vaporization processes of single droplets by Hieftje and Malmstadt[5] gives further promise for the development of optimized systems of flame vaporization and excitation. These developments coupled with the comparative simplicity of spectra produced by flame excitation and the inherent reproducibility of flames for quantitative work, suggest a bright future for flames in the field of environmental analysis.

Arcs. The direct current arc is usually considered to be the most sensitive source for trace element analysis by emission spectroscopy. One reason for this high detection capability resides in the fact that comparatively large samples (100 milligrams or more) can be employed. Most of the current in this type of discharge is carried by the electrons which impact on the anode and quickly elevate it to very high temperatures. This promotes rapid sample vaporization with an attendant high concentration of atoms in the analytical gap.

Typically, nonconducting powders, solution residues, and similar samples are placed in the crater of a supporting graphite or carbon electrode. Three typical electrode geometries for direct current arc analyses are shown in Figure 20-1 (A), (B) and (C). Many other electrode shapes have been employed in direct current arc work.[6] These variations in electrode configuration influence volatilization rates of elements and related aspects of the volatilization-excitation process. The choice of graphite and carbon as materials of construction for electrodes is based on the fact that (1) they are electrically conductive, readily manufactured in high purity, and easily shaped and (2) the carbon vapor produced during use does not depress the excitation characteristics of

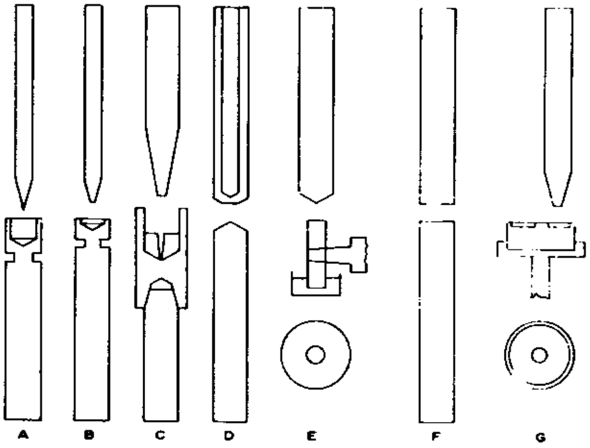

Figure 20-1. Some Typical Electrode Geometries.

the arc since the ionization potential of carbon is greater than that of most elements determined by this method.

One of the major objections to the use of the direct current arc is its tendency toward poor reproducibility in quantitative analysis. If we remember that the sample-containing crater is analogous to a miniature distillation pot, any fixation of the arc at one or a few spots on the anode results in temperature gradients that will promote selective volatilization of the sample. This type of behavior is generally nonreproducible from one burn to the next. The use of "spectroscopic buffers," extensively discussed by Boumans,[1] can greatly improve this situation if the buffer is carefully selected. Such buffers are usually compounds containing elements having low ionization potentials which tend to reduce the effective excitation temperature of the arc plasma and increase the population of neutral atoms. Using various buffers in a free-burning 10-ampere direct current arc in air at atmospheric pressure, Boumans reported a range of temperatures from 5,000 to 6,200°K.

Many of the objectionable features of the direct current arc can be reduced by directing an annular stream of gas upwards around the sample as it is arced. This system, first proposed by Stallwood,[7] reduces arc wander. In addition, it has a tendency to reduce selective volatilization, thus oftentimes improving both precision and accuracy. If an inert gas is employed, the cyanogen bands are eliminated, thereby opening up a region of the spectrum which contains a number of sensitive lines.

Although we frequently go to great lengths to eliminate selective volatilization, sometimes it is possible to take advantage of this phenomena. In this approach, the shutter of the spectrograph is opened only while elements of interest are in the analytical gap. With the overall exposure level reduced, very large samples may be used; and this may produce a significant gain in detection capability. Many examples of this procedure have been described by Ahrens and Taylor.[8]

Occasionally, the addition of certain compounds to the sample can be used to induce chemical reactions which will either promote or reduce selective volatilization. One of the best known examples of this procedure is the carrier-distillation method first described by Scribner and Mullin.[9] A comparatively large sample (100 mg.) is mixed with a carrier such as gallium oxide or silver chloride and then packed into a deep-cratered electrode of the type shown in Figure 20-1 (C). Many investigators also like to put a vent hole in the center of the sample to permit a smooth evolution of gases after the arc is struck. The electrode geometry is especially chosen to reduce heat loss from the sample-containing anode. Volatile impurities are transported into the excitation zone with the carrier while the refractory matrix is left behind.

Spark Discharges. Spark discharges are those in which the energy flow between the electrodes varies in a cyclic fashion, usually with a change of polarity each time the energy flow drops to zero. Because the discharge is being constantly reignited, there is improved random sampling of electrode surfaces. Consequently, this discharge is generally considered to provide better precision but less sensitivity than arc discharges. The poorer sensitivity compared to a direct current arc is largely because the electrodes remain relatively cool, and considerably less sample is consumed. Despite this restriction, spark discharges have been employed with increasing frequency for trace analysis due to their excellent reproducibility. A comprehensive review of the characteristics of spark discharges was published by Walters and Malmstadt.[10]

The most extensive application of spark discharges is for the analysis of metals as self-electrodes. However, powders have been analyzed by blending and compressing with graphite to form conductive briquets. Solutions have been analyzed by a variety of innovative procedures. In the porous cup technique developed by Feldman,[11] a solution slowly percolates through the porous bottom of a hollow electrode [Figure 20-1 (D)]. As the liquid sample seeps through the porous bottom of the electrode, the spark discharge vaporizes and excites the residue to produce an emission spectrum. Another very versatile solution method involves the use of a rotating graphite disc that dips into the solution to be analyzed and transports fresh solution on its periphery into the spark excitation zone [Figue 20-1 (E)].

For very small samples, some solution methods are impractical because of the volume of sample required for analysis. In such situations, residues from the evaporation of these solutions can be analyzed. One of the best known solution residue methods is the copper-spark technique of Fred, Nachtrieb, and Tomkins.[12] A hydrochloric acid solution containing a very small amount of sample (<0.2 mg) is applied to the end of high purity copper rods and dried. The copper rods are then mounted, and the sample is subjected to spark excitation. Excellent detection capabilities are realized with this procedure; but, of course, copper cannot be determined and solvents that react with copper cannot be used. In an attempt to circumvent this limitation, Morris and Pink[13] employed flat-topped graphite electrodes [Figure 20-1 (F)] which had been treated with Apiezon-N grease to render them impervious to solutions. This procedure, called the graphite-spark technique, has exhibited detection capabilities in the nanogram range for several elements. A variation of this approach employs the rotating "platrode" developed by Rozsa and Zeeb[14] in which a graphite disc is substituted as the bottom electrode so that solution volumes up to 0.5 ml can be evaporated [Figure 20-1 (G)].

Plasmas. The plasma jet, sometimes called the gas-stabilized direct current arc, is an excitation source which has been used advantageously for the analysis of solutions.[15,16] In this procedure, the solution is aspirated into a chamber by an inert gas under pressure and then swept through a small orifice into a direct current arc discharge. When the gas flow is increased through the orifice, the electrical conductivity of the jet rises, resulting in a high temperature at the core of the discharge.

The special advantages of this system are the excellent detection capability and the high degree of reproducibility. Precision values are generally much improved over conventional direct current arc excitation.

Another plasma excitation system of special interest is the induction-coupled plasma. In the system described by Dickinson and Fassel,[17] the solution is converted into an aerosol by an ultrasonic generator. A condenser system is employed to desolvate the aerosol particles which are then introduced to the center of a donut-shaped argon plasma in a clear quartz tube. Power is supplied by a high frequency generator operating at 30 MHz. With this system, solutions were introduced at a rate of 0.3 ml/min. For many elements, detection capabilities were in the nanogram/ml range. Since the temperature of this source is on the order of 10,000°K, even the most refractory species are dissociated; and chemical interferences from matrix elements should be drastically reduced. The induction-coupled plasma deserves considerable attention in future methodological development.

Another very unique and potentially useful plasma source has been described by Kleinmann and Svoboda.[18] In this system, the sample is evaporated from a graphite disc which is resistively heated. The evolved vapors are excited by a low voltage, high frequency, induction-coupled discharge in argon. Moderately good detection capabilities were obtained. Since the ideal of separating vaporization and excitation is attained in this source, there is an excellent opportunity to control interferences from elements which make up the bulk of a sample.

Laser Excitation. The analysis of very small areas of samples can be accomplished by emission spectroscopy using a laser to vaporize the sample. This system, first described by Brech and Cross,[19] employs a high intensity pulsed laser beam focused on a spot that may be as small as 10 microns in diameter. With biological and geological specimens, it provides a means of gaining much greater insight into compositional variations than can be attained by bulk analytical systems.

A major problem with the system is the difficulty in obtaining precise quantitative results. Reasons for this difficulty relate to problems in controlling the laser output energy, and the fact that it is extremely difficult to prepare standards for the establishment of calibration curves. Recently, however, Scott and Strasheim[20] have described the use of a Q-switched neodymium laser without an auxiliary excitation system. They obtained promising results in the analysis of aluminum alloys with relative standard deviations in the range of 2% to 4%. Clearly, the ultimate potentialities of laser excitation for emission spectrographic analysis have not been realized.

Resolution of Emitted Radiation. Prisms and diffraction gratings are used to resolve the emitted light from a spectroscopic source into its component wavelengths. A variety of commercial instruments are available with differing geometric arrangements of the necessary optical components. For additional details, the interested reader can consult the recent text by Slavin.[21] Only a few points of special interest in the analysis of industrial hygiene samples will be considered here.

One of the most important properties of a spectrograph is dispersion, usually expressed as the reciprocal linear dispersion in Å/mm. According to Mitchell,[22] "It is in general not the elements to be determined, but the source to be used and the composition of the material to be examined, insofar as its major constituents are concerned, which decide the instrument to be used." When the number of lines produced by the major component is large, the reciprocal linear dispersion of the spectrograph must be small so that lines from the matrix material will not interfere with lines of elements to be determined. Fortunately, the major elements in most biological samples yield relatively simple spectra; and so, a spectrograph of only moderate dispersion is adequate. Of course, the industrial hygienist also encounters samples whose major components yield very complex spectra. For example, a plant processing heavy metals could yield dust samples which would produce extremely complex spectra requiring a large instrument with small reciprocal linear dispersion.

Detection capability can be a very important consideration in the analysis of typical industrial hygiene samples. In those cases where sample size is not limited, dispersion is the most critical factor governing detection limits. In a large spectrograph with low reciprocal linear dispersion, a given amount of background radiation is spread over a large area while the line remains unaffected. Jarrell[23] emphasized that this increase in line-to-background ratio occurs only up to the critical dispersion, i.e., the point at which the slit and line widths are equal.

When the industrial hygienist is interested in analyzing extremely small samples, the absolute quantity of an element is more important than its relative concentration. Mitteldorf[24] has emphasized that the critical consideration here is the speed of the spectrograph (approximately defined as light yield). Thus, we would normally use a small spectrograph of high speed (typically f/10) for micro samples. In contrast, a large spectrograph with optical speed on the order of f/30 might be employed where sample size is not limiting.

Recording Spectral Lines. Spectral lines are recorded either photographically on films and plates or photoelectrically. Emulsions of widely varying speed and resolving power are available to photograph the various wavelength regions of interest. When the investigator wishes to determine elements over a wide concentration range with moderate precision and accuracy, an emulsion of moderate contrast and high speed is selected. For precise quantitative analysis, an emulsion of high contrast is usually preferred.

Direct photoelectric recording of spectral line intensities is considerably more precise than photographic recording and is, therefore, often used for quantitative work. However, direct readers are expensive and sometimes lack the flexibility required for survey analyses. Therefore, it is unlikely that photographic recording will become obsolete in the immediate future.

Quantitative Measurements. In order to do quantitative analysis by emission spectroscopy, it is necessary to estimate the intensity of spectral lines. When lines are recorded photographically, their optical densities can be measured by a microphotometer. In this system, a narrow slit of light is scanned through the spectral line. A photoelectric detector records the decrease in light transmission associated with the blackening on the photographic plate. The photoelectric detector output is recorded as optical density of the spectral line.

Next, optical densities must be translated into relative intensities by means of an emulsion calibration curve. To prepare an emulsion calibration curve, a variety of procedures are used including the use of rotating step sectors and filters with known light transmittances. Several accepted calibration procedures have been carefully described along with worked examples in ASTM Designation E 116.[25]

For high volume repetitive quantitative determinations, direct reading spectrometers are generally employed to reduce the manual effort required. Photoelectric detectors are mounted behind exit slits located in the proper positions to record selected spectral lines. Calculation procedures have also been automated by using computers to handle data reduction.[26,27] Even when spectra are recorded photographically, data reduction can be greatly facilitated via computer handling. Besides speeding up computations, errors are minimized, and precision is frequently improved.

SCOPE

Sample Types

Considering the variety of excitation sources which have been devised, it should be clear that emission spectroscopy provides the capability for detecting traces of most elements in solids, liquids, or gaseous samples. Solid metal specimens can be analyzed directly as self-electrodes, or they may be converted to other forms such as solutions. Inorganic powders can be directly analyzed; or they, too, may be converted to solution form. Solid specimens which contain large amounts of organic matter are usually either wet digested or dry ashed prior to analysis. Otherwise, the rapid combustion of organics may cause vaporization losses and inefficient excitation of the elements to be determined. Despite this fact, some methods have been devised for the direct analysis of organic solids and fluids without ashing. A wide variety of solutions such as natural water and acid digests of samples can be analyzed either by direct solution aspiration or by analysis of the solution residues. Gaseous samples can be analyzed by excitation in hollow cathode discharge tubes or in flowing systems. In short, the diversity of sample types that can be analyzed by emission spectroscopy is one of the great strengths of the method.

Sensitivity

Throughout much of the literature, the terms, sensitivity and detection limit, have been used interchangeably. In this discussion, sensitivity is defined as the ability to discern a small change in concentration of analyte at some specified concentration. Thus, sensitivity is directly correlated with the slope of the analytical curve relating line intensity to analyte concentration. Sensitivity is also inversely related to the reproducibility of line intensity measurement. For high sensitivity, we require a large slope for the analytical curve and a small value for the standard deviation of line intensity.

It should be apparent from the foregoing sections that sensitivity is controlled by a multiplicity of factors in the total analytical procedure. Sample treatments such as selective preconcentration can improve sensitivity. Choice of excitation source, the fundamental properties of the spectrograph and the extent to which its performance is optimized, choice of detector, and the method of data manipulation all affect sensitivity.

Concentration Ranges

Although there is no hard and fast rule which precludes using emission spectroscopy for the determination of high concentrations of elements, the most advantageous concentration range lies below 10 percent. In fact, the preponderance of applications deal with determinations between 1 percent and the limit of detection.

Limit of detection is defined here as the smallest quantity or concentration of analyte that can be detected "with certainty." Apparently, then, limit of detection is merely a special case of sensitivity which depends on an ability to distinguish a difference in line intensity for a small increment of analyte in comparison to the blank signal. Thus, the limit of detection is inversely correlated with sensitivity. The limit of detection also depends on the definition of "with certainty." Although it is widely accepted that a statistical definition should be used, there is little agreement on the proper confidence level. To assume that a single value for the confidence level is correct seems naive. It is much more realistic to allow each investigator to choose a probability level that suits the particular requirements of the problem at hand.

Some specific procedures necessary to achieve improved detection limits have been discussed by DeKalb et al.[28] for both photographic and photoelectric sensors. It must be emphasized, however, that many of these detection limits are reported for ideal situations in which there is no matrix interference or other limiting characteristic. In addition, many different definitions of the detection limit have been employed by various investigators, thereby making direct comparisons very difficult. It should also be remembered that limits of detection do not represent concentrations that can be determined with the same quantitative precision and accuracy expected for higher concentrations. In general, the lower limits for good quantitative precision are approximately 10 times the detection limits.

While much can be accomplished through the selection of optimum instrumental conditions, sensitivity and detection limits can also be enhanced by sample preparation procedures that provide an enrichment of the analyte. Some typical procedures are described in Chapter 18 of this syllabus. Aside from the extra effort required in sample preparation, a major precaution with enrichment procedures is the possible introduction of impurities from chemical reagents which obscure the true pattern of variation present in the original samples.

Precision and Accuracy

Precision is defined here as the extent of agreement of a series of measurements with their average, frequently measured by the standard deviation. It is essential to express the conditions under which the data have been obtained. Commonly, precision is expressed as the percent relative standard deviation (sometimes called coefficient of variation).

If we accept that a realistic value for the precision of a total analytical method applied to a given material should include components from the sampling step, the sample preparation step, and the measurement step, then the difficulty in making general statements for different methods is obvious. Nonetheless, it is generally conceded that the precision of emission spectroscopic techniques is superior to chemical methods at very low concentrations and inferior to chemical methods at concentrations much above 1 percent.

Usually, methods that employ solutions for the final intensity measurement give better precision than direct methods with solids. One reason for this difference is that larger samples are usually employed for solution methods. Under ideal conditions, percent relative standard deviations of ± 1% can be obtained with solutions except when impurity concentrations approach their detection limits. Good reproducibility is also attained for the analysis of metals as self-electrodes. With the direct excitation of powdered solids, sample heterogeneity becomes more important; and percent relative standard deviations of ± 5 to 10% are more typical. For survey procedures which cannot be optimized for each element determined, percent relative standard deviations of ± 25% or larger might be considered acceptable.

Accuracy is defined as a quantitative measure of the variability associated with the relating of an analytical result with what is assumed to be the true value. Strictly speaking, accuracy can never be exactly measured because true values are never known. However, when primary standards are available, the accuracy can be specified within acceptable limits.

Since quantitative emission spectroscopy requires the establishment of an analytical calibration curve based on standard samples, the accuracy is limited by the quality of the available standards. The precision of a method is sometimes thought to be an estimate of accuracy. However, a method can easily yield very precise but highly inaccurate results if systematic error is present. For example, a common misconception is that synthetic solution standards obviate the need for primary standards in the analysis of miscellaneous materials which can be converted to solution form. Unfortunately, this concept overlooks all of the systematic errors that can occur while converting samples to solutions.[29] The recent activity of the National Bureau of Standards in the preparation of standard reference materials certified for trace amounts of different elements in matrices such as orchard leaves, beef liver, and serum will be of tremendous help to the emission spectroscopist concerned with the accuracy of his procedures.[30]

STEPS OF A QUANTITATIVE METHOD

The first step in any quantitative analysis by emission spectroscopy is to clearly define the problem by designating the elements to be determined and the expected concentration ranges. Any special aspects of the sample such as its major element composition, its quantity, and its physical form should also be noted. Reference standards are required which are similar, both chemically and physically, to the samples to be analyzed. For example, if we wish to determine the concentration of several trace metals in water residues in which the matrix is a mixture of calcium, potassium, magnesium, and sodium salts, we normally require standards with a matrix of these same salts to match volatilization-excitation behavior. It may even be necessary to alter the ratios of the salts in the standards to match particular water samples. Lacking standards of similar physical and chemical composition, the samples must be modified to correspond with standards that are available. This may entail conversion to solutions, inorganic powders, or some related operation.

Once the physical form of samples and standards has been decided and the analytical requirements specified, it should be possible to make an optimum choice of the excitation system, assuming that several are available. Similarly, we should attempt to insure that the spectrograph will provide sufficient resolving power and adequate speed for the detection and estimation of the elements to be determined. This means that we must be able to locate lines of the analyte elements which are free from interferences by lines of the matrix elements. Further, these lines must be sufficiently sensitive to provide measurable optical densities down to the concentration levels required by the analysis.

In prior discussions, we have inferred that quantitative analysis involves only the construction of an analytical calibration curve relating intensity of the line of an element to be determined to the known amount of that element in a series of standards. However, because of the multitude of factors that affect the total amount of light emitted by a given weight of an element, this direct approach has usually not provided adequate precision and accuracy. To circumvent this difficulty, the principle of internal standardization is employed. In this procedure, concentration of the element to be determined is measured in terms of the ratio of the intensity of the analysis line to the intensity of a "homologous" line of another element present in fixed concentration in all samples and standards. The internal standard element may be a major component of the matrix which is present in invariant concentration. Alternatively, it may be an element which is absent in the samples and which has been added in constant amount from an external source. In this manner, uncontrollable fluctuations such as variations in excitation efficiency that affect both lines to a similar extent will not alter the intensity ratio between the lines. Unfortunately, it is usually impossible to find line pairs whose intensity ratios are completely insensitive to changes in chemical and physical composition of the sample. However, the literature provides references to many line pairs which are sufficiently insensitive to extraneous influences to permit excellent precision in quantitative work.

After preparation of samples and standards, they are excited in random order and recorded on a photographic plate or photoelectrically. If the lines are recorded photographically, their optical densities are measured and converted to relative intensities by means of an emulsion calibration curve. The intensity ratios of analytical lines relative to the selected internal standard lines are calculated and plotted on log-log paper versus the respective concentrations of the elements in the standards. Intensity ratios for the unknown concentrations in the samples are then read from these calibration curves.

Analytical calibration curves must be frequently checked. Day-to-day variations in atmospheric conditions will exert sufficient influence on excitation processes and photographic emulsions to cause significant curve shifts. The extent to which an investigator must check for curve shifts and recalibrate is partially dependent on the required precision and accuracy of the analyses being performed. For a summary of recommendations, the ASTM Designation E305-67 titled "Establishing and Controlling Spectrochemical Analytical Curves" should be consulted.[31]

APPLICATIONS IN INDUSTRIAL HYGIENE

Analysis of Biological Tissues and Fluids

The work of Tipton and Stewart[32] is a typical example of a dry ash-direct current arc excitation procedure for surveying trace element contents of biological tissues and fluids. Samples of food, urine, and feces are dried and ashed at 550°C after treatment with double distilled sulfuric acid. This treatment produces a clean ash of mixed sulfates and oxides. The ash is combined with a graphite buffer containing 2,000 parts per million of palladium which serves as the internal standard. Synthetic standards of similar composition are prepared from inorganic materials. The elements Ag, Al, B, Ba, Be, Cr, Co, Cu, Fe, Mn, Mo, Ni, Pb, Sn, Sr, Ti, V, Zn, and Zr are determined at concentrations down to 1 part per million or less in a few cases with typical percent relative standard deviations on the order of ± 10%.

A typical procedure employing wet ashing of biological fluids prior to spectroscopic analysis is described by Niedermeier et al.[33] In this procedure, 2 ml of blood serum are digested with high purity nitric and perchloric acid. A battery of samples is treated simultaneously using a number of digestion tubes in a constant temperature block which can be maintained at 130°C. After ashing, the excess acid is evaporated; and the residue is dissolved in ammonium chloride solution which serves as a spectroscopic buffer. An aliquot of the solution is transferred to a graphite electrode and evaporated to dryness in a vacuum desiccator. Synthetic standards are prepared in a matrix solution with composition closely approximating that of normal human blood serum. Excitation is accomplished by a 10-ampere direct current arc. Selected lines of Cu, Fe, Al, Ba, Mn, Ni, Cs, Sn, Sr, Cr, Zn, Pb, Mo and Cd are monitored with a direct reading emission spectrometer. Data analysis is accomplished by an IBM 7040 computer.

For rapid survey purposes, the procedure described by Bedrosian et al.[34] is especially attractive because ashing of the sample is not required. Materials such as animal tissue, blood serum, stool, bone, and plant leaves are dried. Twenty-five mg of samples are blended with graphite containing lutetium and yttrium as internal standards. The blended mixture is formed into a 3/16 inch diameter pellet using a small hand press. The pellet is placed in a graphite electrode, and a 1 mm diameter vent hole is placed in the center of the pellet. Electrodes are mounted in a Stallwood jet, and a gas mixture of 20% oxygen and 80% helium is used while the samples are excited by a 25-ampere direct current arc. They detected 26 elements in these various matrices at 1 part per million or less. Quantitation is accomplished using standards containing known concentrations of the trace metals in a matrix of p-nitrobenzene-azo-resorcinol which serves to simulate the organic matrix of samples being analyzed. The authors reported percent relative standard deviations of ± 15% or less.

Water Samples

The determination of trace metals in natural waters is of great interest from a toxicological point of view. An excellent survey procedure for the determination of 19 minor elements in water has been described by Kopp and Kroner.[35] In this procedure water samples are filtered through a 0.45-micron membrane filter. Total dissolved solids are determined, and a volume of sample is selected to contain 100 mg of solids when concentrated to 5 ml. A portion of this concentrate is placed in a porcelain combustion boat and analyzed in triplicate using a rotating disc electrode and high voltage spark excitation. Standard solutions for construction of the analytical calibration curves are prepared using known amounts of the elements to be determined in a matrix of sodium, potassium, calcium and magnesium in proportions approximating the average composition of U. S. waters. Line intensities are recorded photoelectrically, and background is used as an internal standard. The concentration range is from 0.01 to 100 parts per million in the concentrated solution. Thus, the lower limits for the original samples depend on the degree of concentration employed to get 100 mg of dissolved solids. Precision expressed as the percent relative standard deviation was on the order of ± 5%. Recoveries from known additions varied from 80% to 113%.

Analysis of Air Samples

Not all spectrochemical analytical procedures are devised to determine multiple elements simultaneously. For example, O'Neil[36] described a procedure for the determination of beryllium in airborne dust. A high volume air sampler is used, and the sample is collected on Whatman No. 41 filter paper. The filter is ignited in a platinum crucible, and the ash weighed and mixed in definite proportions with an internal standard (lutetium) and graphite. The mixture is excited in an 11-ampere direct current arc and burned to completion. The author reported being able to detect 0.1 nanogram of beryllium in an electrode. Acceptable precision and accuracy was reported.

Of course, procedures have also been described for determining a large number of trace elements in air particulates. For example, the procedure by Keenan and Byers[37] permits the determination of 20 elements collected on paper filters.

SUMMARY

Emission spectroscopy provides an effective analytical technique as both a survey method and as a quantitative analysis tool. The applicability of this technique is being continually extended in the industrial hygiene field.

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