238

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Survey of Various Approaches to the Chemical Analysis of Environmentally Important Materials

Bernard Greifer and John K. Taylor

National Bureau of Standards
Department of Commerce
Washington, D. C. 20234

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Final Report

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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary
NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

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Bernard Greifer and John K. Taylor, Editors

Report to

Office of Research and Monitoring
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TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

PAGE

ATOMIC EMISSION SPECTROSCOPY (Continued)

PAGE

POTENTIOMETRY (ION-SELECTIVE ELECTRODES) (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

PAGE

ATOMIC EMISSION SPECTROSCOPY

VOLTAMMETRY (POLAROGRAPHY)

LIST OF FIGURES

PAGE

INTRODUCTION

X-RAY FLUORESCENCE AND ELECTRON MICROPROBE

SURVEY OF VARIOUS APPROACHES TO THE CHEMICAL ANALYSIS OF ENVIRONMENTALLY IMPORTANT MATERIALS

ABSTRACT

Various approaches to the chemical analysis of heavy industry process materials and effluents for trace element constituents that might contribute to environmental pollution are summarized.

The capabilities and costs of nuclear methods, spark source mass spectrometry, x-ray fluorescence and electron microprobe spectrometry, atomic absorption spectrometry, absorption spectrophotometry, atomic emission spectroscopy, voltammetry (polarography) and potentiometry (ion-selective electrodes) for determining traces (less than 100 parts per million) of mercury, beryllium, cadmium, arsenic, vanadium, manganese, nickel, antimony, chromium, zinc, copper, lead, selenium, boron, fluorine, lithium, silver, tin, iron, strontium, sodium, potassium, calcium, silicon, magnesium, uranium, and thorium in such matrices as fly ash, coal, oil, ores, minerals, metals, alloys, organometallics, incinerator particulates, slurry streams, and feeds to and from sedimentation processes have been assessed.

The report includes a critically selected bibliography of the current literature.

Key words: Air pollution; atomic absorption; electron microprobe; emission spectroscopy; environmental analysis; industrial effluents; ion-selective electrodes; nuclear activation analysis; particulate analysis; polarography; spark source mass spectrometry; spectrophotometry; trace elements; water pollution; x-ray fluorescence.

CHAPTER 1

INTRODUCTION

Bernard Greifer

1. REPORT FORMAT

This report is an evaluation of various approaches to the chemical analysis of heavy industry process materials and waste products for constituents that may find their way into the environment and be considered pollutants. The applicability and costs of suitable methods of measuring the trace metal content (less than 100 ppm) of industrial process feeds, product streams, and effluents are presented for comparison so that the optimum analytical support programs for particular situations can be selected from among the available alternatives.

Heavy industrial processes have come under scrutiny as contributors to environmental contamination. While sulfur dioxide and particulate emissions have been investigated extensively, the trace elements in these and other effluents have been relatively unexplored. These trace elements may be a source of valuable byproducts that could be recovered, or they may constitute a toxic hazard that should be removed; but they ought not to remain an unknown quantity. Modern instrumental methods of analysis have the capability to determine the trace elements in industrial effluents at a reasonable cost. This report summarizes current procedures suitable for the analysis of these and similar materials.

The information provided is based on a bibliographic survey and evaluation of the current literature by members of the staff of the Analytical Chemistry Division, Institute for Materials Research, of the National Bureau of Standards. The work was carried out under an interagency agreement between the Department of Commerce and the Environmental Protection Agency dated June, 1972.

A. Scope of Report

The report assesses the capability and costs of various methods of determining the concentration of trace elements (< 100 ppm) in the following basic sample matrices: fly ash, coal, oil, ores, minerals, metals, alloys, organometallics, incinerator particulates, slurry streams, and feeds to and from sedimentation processes. As the occasion presents itself, additional matrices may be mentioned, as water, sediments and coagulates.

The trace elements of analytical interest include: mercury, beryllium, cadmium, arsenic, vanadium, manganese, nickel, antimony, chromium, zinc, copper, lead, selenium, boron, fluorine, lithium, silver, tin, iron, strontium, sodium, potassium, calcium, silicon, magnesium, uranium, and thorium. In this listing the elements may be considered as major or minor constituents according to their relative concentrations in the matrix materials, but most of the attention will be directed toward elements present at or below the 100 ppm (100 μg/g) level.

The analytical methods included in this review embrace nuclear methods, mass spectrometric methods, x-ray, optical, and electrometric methods of analysis, specifically:

1. Nuclear methods
2. Spark source mass spectrometry
3. X-ray fluorescence and electron microprobe spectrometry
4. Atomic absorption spectrometry
5. Absorption spectrophotometry
6. Atomic emission spectroscopy
7. Voltammetry (polarography) and potentiometry (ion-selective electrodes)

The methods considered are those which are capable of rapidly and accurately determining trace elements in a variety of materials with a minimum of sample manipulation. Analytical methods requiring long and careful sample processing such as isotope-dilution mass spectrometry have not been included in this survey because of their prohibitively high labor cost and slow accumulation of analytical data. For this same reason, wet chemical procedures are considered only as they are involved with instrumental methods such as spectrophotometry.

The performance of the analytical methods is considered from the viewpoint of their capability to carry out the required trace element determinations on the matrices of interest, at a reasonable cost. The parameters of interest include:

1. Instrumentation requirement
2. Detection limit
3. Accuracy
4. Sample preparation
5. Sample size
6. Manpower skills requirement
7. Cost per analysis

The performance parameters are listed in no special order. The information for each analytical method is taken from the literature wherever possible, and supplemented from the personal experience of the NBS staff members in other cases where literature references are not available. These performance parameters provide guidelines for comparing the various analytical methods but they do not contain sufficient information to permit a decision to be made that one method is superior to another in a specific application.

B. Organization of Report

The report is divided into chapters describing the analytical methods under consideration. The chapters contain bibliographies citing general sources of information and specific references keyed to the elements of interest in the matrices being analyzed. Tables summarizing the analysis of each element according to detection limit, cost, and other performance parameters are included for each method. The accompanying chapter texts provide comments and connecting narrative.

Various indexes are provided to facilitate access to the tabular information pertaining to the determination of each trace element likely to be present in the matrix materials. Details of methods of analysis of specific matrices, or determination of specific elements, or costs of such determinations may be located in the chapter texts, tables, and bibliographies by reference to these indexes or to the Table of Contents.

The sample matrices are grouped differently in each chapter depending on the common characteristics of importance to each analytical method. For example, one analytical method may group the matrices according to their silica content or their solubility in mineral acids, while another method may find a common denominator to be the organic content. The table headings provide entry into the analytical information and the references.

Costs are listed in the tables as the cost of analyzing a single sample. In some cases each element is the sole constituent being determined, as in atomic absorption spectrometry; and in other cases each element is considered to be one of a group of elements being determined sequentially, as with x-ray fluorescence, or simultaneously on the same sample, as with spark source mass spectrometry. The costs of trace element determinations will generally fall between the two extremes of low-cost multi-element survey methods and high-cost single-element determinations. Also, the cost per sample for large numbers of routine determinations can be expected to be less than indicated in the tables. Accordingly, the tabulated values should be considered as guidelines to maximum reasonable costs when the analyses are done by experienced, trained analysts.

Tables in each chapter list performance parameters for each method of analysis according to matrices and trace elements of interest. Where possible, information is provided on sample sizes required, analytical accuracies expected, and costs of determining elements present at concentrations about 1, 10, or 100 ppm. Some methods of analysis not particularly suited for trace determinations (e.g. x-ray fluorescence) are described for element concentrations considerably above 100 ppm in order to present a complete picture of the methods' capabilities.

The tabulated information and supporting references are presented without judgments as to the relative merits of the various analytical instruments and procedures. Decisions regarding the suitability of alternative methods for trace element determinations should be based on experiences with real samples.

2. TRACE ANALYSIS OF REAL SAMPLES

A. Materials Balances

An assessment of the environmental impact of an industrial process or subprocess requires analytical data of several kinds. Figure 1 is a flow diagram showing the different chemical analyses that might be used to monitor the material flow in and out of a typical process. Ores and scrap metals are analyzed before they are smelted in a blast furnace, and the commercial metals and crude intermediates are analyzed as products. The effluent gases, solids, and liquids are analyzed before being recycled, recovered as byproducts, or treated and released to the environment as wastes. As indicated in Figure 1, these data might be expected to indicate a materials balance because all of the inputs and outputs are being analyzed. However, achieving a complete materials balance among all of the trace constituents may be a difficult undertaking, especially if trace elements interchange between process materials and walls of pipes and vessels, or if there are minute losses or additions from the environment (i.e. contamination). Many engineers would be pleased with a product purity of 99.9 percent, but the analytical chemist sees 1,000 ppm of other constituents in this product. This difference in outlook between the engineering viewpoint and the chemist viewpoint is crucial to an understanding of the relative merits of the different analytical methods.

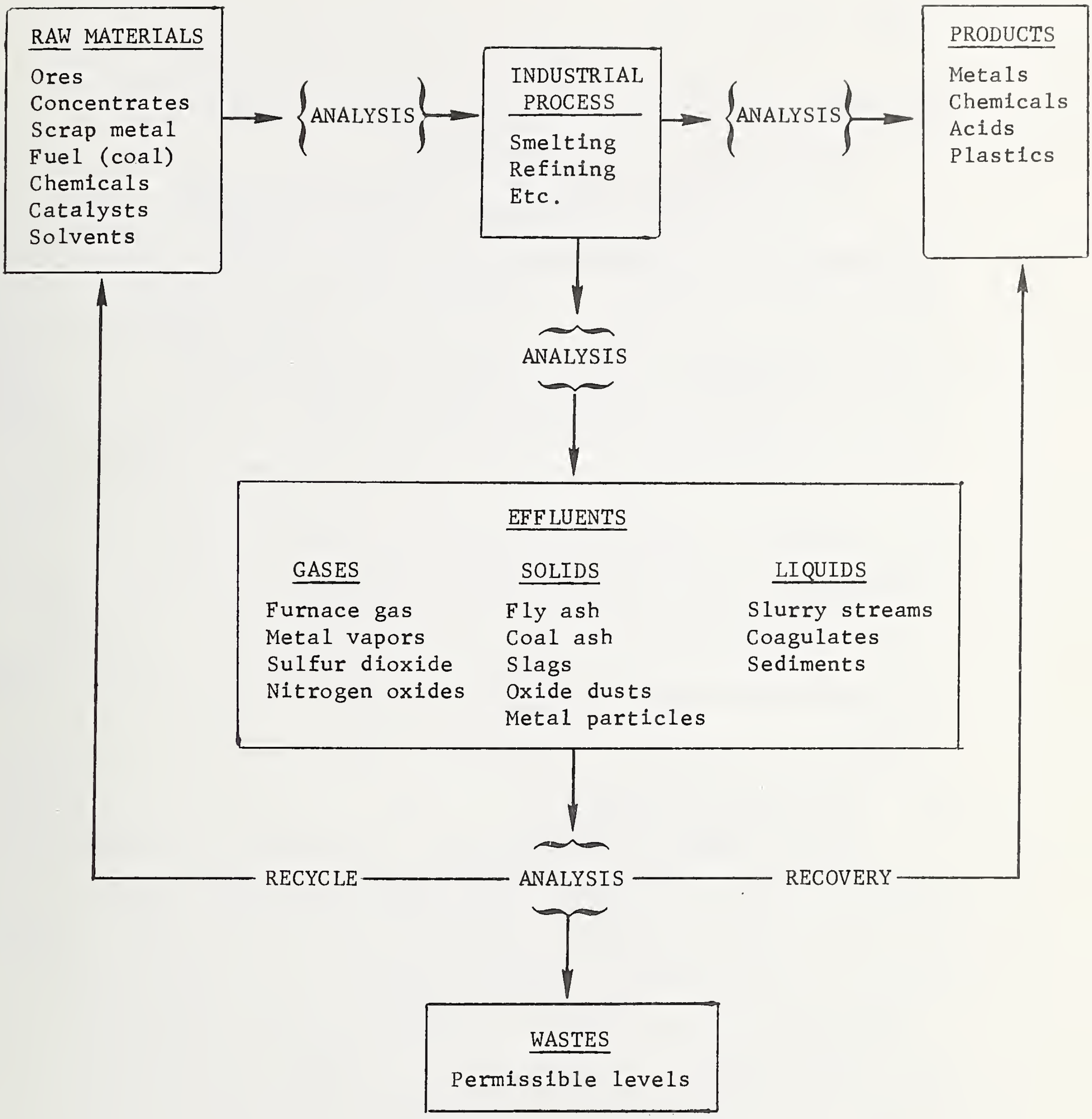

Figure 1. Applications of trace element analysis to monitoring materials, process streams, and effluents of a typical industrial process.

The materials balance which is complete to 100.0 percent from an engineering viewpoint is not good enough to account for trace elements; it must be complete to 100.0000 percent to account for a 1 ppm constituent.

For a material balance of trace constituents to be reliable, the analyses must be not only precise, they must above all be accurate. A small error in the analysis of a major component of the raw material could lead to a serious error of judgment regarding the need for, or the reliability of the analyses in the final products, or waste products, or emissions. Accurate measurements are best ensured when dependable, evaluated methods of analysis are used, and requisite calibrations made with reference materials are interspersed in the course of the analyses to provide quality control.

B. Matrices of Interest

Trace element analyses can be carried out routinely after suitable procedures have been established and the requisite instrumentation installed. The materials under consideration for trace determination may be thought of primarily among the products and effluents if the main concern is environmental contamination; however, ores, fuels, and other process inputs should be included in the interest of a suitable materials balance. The diversity of materials to be analyzed is demonstrated in this listing of matrices which may contain trace elements of environmental importance:

1. Raw materials such as ores, concentrates, scrap metals, coal and coke, chemicals, catalysts.

2. Products and intermediates including commercial metal, slags, sinters, blister metal, and bullion.

3. Gaseous emissions including acid mists, fly ash and other particulates as metallic and metal-oxide dusts, partly burned fuels.

4. Process waste waters including coagulates, sediments, and sludges produced in the course of upgrading effluents for pollution control.

5. Plant working environment including dusts, filters, water and solvents, lubricating oils, vapors from molten metals.

The number and variety of sample materials and their expected complexity and inhomogeneity can give rise to difficult problems in sample collection and analysis. Just as chemical analysis is a specialized field, the sampling of process streams requires sophisticated planning by engineering specialists to assure that the samples are representative of the materials of interest. Since such an assurance is vital to the success of the trace element determinations, some of the problems encountered in sampling will be discussed.

C. Sampling

One of the most important considerations in chemical analysis is the assurance that the samples in the laboratory are truly representative of the bulk materials from which they have been taken; and this is especially true in the case of trace determinations. It is obvious that analysis can give information only about the particular samples in the laboratory. If these are not the same composition as the slags, sediments, process streams, etc. which they purport to represent, then the chemical results can have no value whatever and may even be misleading. Obtaining a representative sample may not be a simple matter. The matrix materials are typically inhomogeneous, consisting of two or more poorly mixed phases most of the time. The trace element compositions may be changing continually since they depend upon the interaction of a great many process variables, e.g. impurities in the ores, process side reactions, transfer of material to or from vessel walls and pipes, loss of volatile elements during roasting, transfer of material to or from filters; all these may affect the trace element content of the matrix materials.

Sampling of heterogeneous combinations of liquids, solids, and gases such as gas-borne particulates, mists, slurries, and sludges requires careful planning. It is essential that the number and selection of samples taken for analysis be such as to assure that all the trace elements present in the matrices are represented in their correct concentrations. The problems encountered in sampling process streams for trace constituents may arise from such sources as (1) the inhomogeneity of the matrix materials, (2) composition changes with time or some process variable, (3) sample alteration during sampling and transport to the receiver, (4) sample alteration within the receiver, and (5) inefficient collectors which do not capture 100 percent of the trace elements along with the samples. Collection of representative samples from process streams may require the combined efforts of engineering specialists in stream analysis, fluid mechanics, chemical reactions, corrosion, and materials separation to name a few disciplines.

It is important to understand why the sampling is being done, what streams and what phases in the streams are to be sampled, where are the best places to sample, when are the best times to sample, how big a sample to take, how long a sampling time, how to collect and retain all the trace elements. [1]

An often overlooked factor in sampling is the detailed and unambiguous identification of analytical samples. Such vital information as date, time, and location of sampling should be recorded. Other pertinent information such as process parameters at the time of sampling, and even the then-existing environmental conditions may be of importance in many cases to a proper interpretation of the analytical data. The name of the person taking the sample, and reference to the notebook or log sheet should also be indicated. All of these matters assume special importance when legal considerations may be involved.

The analytical chemist ordinarly requires only a part of the sample collected. In this event it is imperative that the portion used for analysis be representative of the sample submitted to the laboratory. Trained analytical chemists are aware of such matters, but the availability of analytical instruments that can be used by laymen prompts this note of caution. Even the trained analyst needs to be reminded to properly identify each sample analyzed and document the experimental conditions used. Calibration procedures and quality control measures should be recorded to provide authentication which might be needed at a later date. In some cases a bank of analyzed samples may be retained for further analysis, for verification, for later reference, or for other purposes.

Since the analytical chemist has no control over the samples before they reach the laboratory, the forthcoming discussions of instrumental chemical analysis will assume that the samples presented for analysis have been obtained knowledgeably and are free from losses or outside contamination.

D. Choice of Analytical Method

Although the performance parameters which comprise the bulk of the tabulated information seem to provide a basis for comparison of the relative merits of the alternative methods of analysis, it is possible that such a comparison might have little application to the real world of dirty samples and fallible people. In fact, it may be generally impossible to decide a priori that one method will be superior to another in a specific situation, because of the numerous subjective considerations which cannot be accounted for, in a report of this type. The rationale behind the choice of performance parameters establishes the general acceptability of the analytical methods according to accepted standards of accuracy, detection limits, analytical costs, etc. However, there are many opportunities for experimental error and operator bias which may be caused by the effects of the matrix constituents themselves on the analyses; or by differences in reagents and standards used by the various laboratories; or by the ability of analysts to obtain the optimum results with their instruments and operating procedures; or the extent to which the samples reflect the actual bulk matrix compositions, and so on.

The "best" methods of analysis will be those that perform most reliably in the actual analysis of real samples. Such methods probably cannot be identified until a body of analytical results is accumulated. It is realistic to acknowledge that the "best" methods often are those with which the laboratories have the greatest experience. New and unfamiliar analytical methods require an investigative or break-in period whose cost must either be recovered through volume analyses or considered a worthwhile investment in improved technological capability, before such new methods are adopted. The value of this report and other compendiums of analytical methods [2] lies in their utility as guidelines to show what others have done to solve similar problems in trace analysis. Judgments as to what can be done in specific situations should be based on careful observation of test results.

REFERENCES

[1] Fair, J. R., Crocker, B. B., and Null, H. R., Sampling and Analyzing Trace Quantities, Chem. Engineering 79, 146 (1972).

[2] Pinta, M., "Detection and Determination of Trace Elements," original edition Dunod, Paris (1962) in French. English edition, Ann Arbor Science Publishers, Ann Arbor, Michigan, Fourth printing (1972).

CHAPTER 2

NUCLEAR METHODS

Donald A. Becker

1. INTRODUCTION

Nuclear methods of analysis have for many years been deeply involved in the analysis of trace levels of numerous elements in a wide variety of sample matrices. This chapter lists the capabilities of the various nuclear methods and provides references to demonstrate their feasibility. However, since most nuclear techniques depend more on the specific elements present in the sample, rather than the broad category of matrix type, no specific matrix differentiation has been made in the accompanying table. Some discussions of the individual matrices of interest are included under Section 3.

2. NUCLEAR METHODS

The broad category of nuclear methods includes almost all methods which depend upon the measurement of a radioisotope resulting from an irradiation process. A brief description of the more important methods presently in use follows.

A. AS - Activation Spectrometry (Instrumental Neutron Activation Analysis)

This is the method of choice if sufficient sensitivity and specificity are available. In this technique, a sample is irradiated in a neutron source (usually a nuclear reactor, to obtain the required sensitivity) for a period of time, and, after withdrawing the sample, the resulting induced radioactivity is observed. This radioactivity is usually detected and quantitated using a high resolution lithium-drifted germanium semiconductor detector [Ge(Li)] for greatest specificity. In this technique, each radioisotope may be uniquely identified through the observation of a.) its gamma-ray energy; b.) its half-life; and c.) its peak ratios (if it has two or more gamma-ray peaks). It is limited primarily by the total radioactivity induced in the sample under evaluation, and often long decay times are required for many elements. However, it is usually possible to determine many elements simultaneously with one or two irradiations and 2 or 4 counts of a particular sample and associated standards.

B. NAA - Neutron Activation Analysis

This method is similar to the previous technique, except that a radiochemical separation can be employed after irradiation, but before measuring the radioactivity. This separation, if done competently, can remove all or most of the interfering radioactivities while retaining all or a known portion of the radioisotope(s) of interest. Thus, while additional effort is required for the separation, the resulting product is one of a few radioisotopes of interest with little or no other interfering radioactivities. Thus, it is usually possible to obtain maximum sensitivity along with high precision and accuracy with this technique.

C. FNAA - Fast Neutron Activation Analysis

This is another method of activation analysis in which fast neutrons are used as the irradiation source. This fast neutron source could be a Cockcroft-Walton neutron generator producing 14 MeV neutrons, another type of particle accelerator used for generating fast neutrons, or a radioisotope source such as californium-252, producing neutrons by spontaneous fission with energies peaking around 2-3 MeV. However, this technique is seldom used for trace analysis due to a lack of sensitivity caused primarily by the relatively low fast neutron fluxes currently available.

D. CPAA - Charged Particle Activation Analysis

This method of activation analysis depends upon the use of radioisotopes produced in the sample by a charged particle beam from accelerators such as a tandem-Van de Graaf or a cyclotron. This method has the capability of detecting several elements difficult to determine by other nuclear methods, and thus has found some limited usefulness. The technique is limited to a great extent by the nature of its irradiation beam, since it can penetrate to only a few microns depth in the sample. Thus, while found to have great applicability in the field of surface analysis, it is quite limited for the types of samples under consideration here.

E. PAA - Photon Activation Analysis

The method of photon activation analysis utilizes the bremsstrahlung radiation produced by the deceleration of very energetic electrons in a high Z material. One excellent source of such radiation is the Linear Electron Accelerator, or LINAC. These high energy photons are very penetrating, thus producing an irradiation source quite useful for several elements, especially those which are difficult to determine by neutron activation analysis. This technique also uses a Ge(Li) detector system for counting, and can also have a radiochemical separation step included in the analysis. Two of the important disadvantages, however, include the lack of generally available LINAC's and the general similarity of gamma-ray energies of the radioisotopes produced by the prevalent (γ,n) nuclear reactions (usually positron emitters).

F. NTT - Nuclear Track Technique

The nuclear track technique makes use of the fission or alpha particle decay of a nucleus undergoing neutron bombardment. If a smooth surface of the sample or a solution of the sample is placed in intimate contact with a special type of plastic, then irradiated (usually with thermal neutrons), several elements produce a track in the plastic which can then be chemically etched and counted microscopically. At present, of the elements of interest here, only boron and uranium can be determined by this technique.

G. IDA - Isotope Dilution Analysis

A number of elements can also be determined using the technique of isotope dilution analysis. This heading includes both isotope dilution analysis and its related technique of substoichiometric isotope dilution analysis. In these methods, a radioisotope of the element of interest with known specific activity is added to the sample, after which all or a portion of the "diluted" element is separated from the sample. The changed specific activity of the separated radioisotope allows the calculation of the concentration of the element in the sample. This technique is listed in Table 1 as a secondary method for several elements.[a]

3. ANALYTICAL APPLICATION TO SPECIFIC MATERIALS

The applicability of nuclear methods for the analysis of fly ash, coal, oil, ores, minerals, metals, alloys, organometallics, incinerator particulates, slurry streams, feeds to/from flotation processes, and sediments in flotation processes has been investigated. It does not seem to be feasible to consider each of these materials separately for all of the elements of interest. Very few papers have been published for these materials even though these methods, especially neutron activation analysis, are eminently suitable for most of the elements in all of the matrices. Thus, only an overview of the different sample matrices will be given here, with some references to specific publications, if available. It must also be remembered, however, that dissolution of the sample after irradiation, with an appropriate

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[a] This is not to be confused with Isotope Dilution Mass Spectrometry which uses enriched stable isotopes as tracers, rather than radioactive isotopes.

radiochemical separation of the element of interest, will yield a determination which is essentially similar for all sample matrices. This is not only possible, but is currently being done in the NBS laboratory as well as many other activation analysis laboratories. This fact, coupled with the ability to verify radioisotopic purity by at least two and possibly three different parameters (i.e., gamma-ray energy, half-life, and peak-ratios) enables reliable analytical data to be obtained for most elements for almost all types of samples.

A. Fly Ash

The primary difficulty in the analysis of fly ash is the high radioactivity level resulting from neutron irradiation. However, since impurity levels are also generally high, the sensitivity loss should not be a problem. Many elements can be determined non-destructively, however, the shortlived radioisotopes (e.g., calcium, magnesium, vanadium) may be impossible to detect at low concentrations. This material can be dissolved in acid mixtures and the element(s) of interest separated, with some increase in cost but with much improved sensitivity. Unfortunately, very little analytical data has been published on fly ash.

B. Coal

This matrix is elementally similar to biological materials, and thus can be tentatively considered in terms of neutron activation analysis results on human tissue (86) and botanical samples (87). In the first publication 30 elements were determined in individual samples by radiochemical separations and gamma-ray spectrometry (86). In the second publication 15 elements were determined non-destructively in samples of dried kale leaves. Again, sample dissolution is simple and separations can be performed to improve the sensitivity and specificity for individual elements or small groups of elements. Many additional activation analysis references are available for trace element analyses in biomedical samples (90,91,92), but only one was found in which a coal was the sample matrix (68).

C. Oil

The activation analysis of oil samples has been demonstrated several times, notably the determination of 13 trace elements by AS in crude petroleum (81), and the systematic determination of 11 trace elements in crude oils, distillation fractions, asphalts, etc., by NAA with radiochemical separations (88). In this latter paper, comparisons were made for some elements with results by other analytical techniques, and precisions of ±10 percent claimed for the NAA results. Additional papers present work on the characterization of marine oil pollution sources by AS (89,97).

D. Ores and Minerals

The activation analysis technique has been applied to large numbers of geological type samples (93,94,95) and to some ore and ore processing product samples (96). In one case, a single sample weighing less than one gram was analyzed by neutron activation with radiochemical separations, and 39 elements were determined with precisions of better than ±5 percent claimed for over half of the elements (95). In a second situation, a neutron generator (FNAA) was used to activate samples and rapid, nondestructive analyses were made for several elements with sensitivities of about 1 mg (96). In an ore and mineral type of sample, the capability of any nondestructive activation technique depends to a significant extent on the concentration of other elements in the matrix. Thus, some preliminary evaluation will usually have to be made before an established analytical procedure can be applied.

E. Metals and Alloys

Much analytical data has been published on the activation analysis of trace elements in metals and alloys. Several particularly useful references other than those from Table 2 are included here (98,99,100). The ease of analysis depends significantly on the activation of the matrix material. Thus, much of the work reported in the literature has been made on sample matrices which are relatively easy, such as aluminum, iron, lead and bismuth. Metals and alloys which activate strongly (such as manganese, copper, gold, antimoy) or fission under neutron irradiation (such as uranium or thorium) are much more difficult to analyze for trace element concentrations.

F. Organometallics

Organometallics have been analyzed by activation analysis for major constituents (101,102), but not often for trace contaminants. This is most likely due to a lack of interest in trace element information, since thermal neutron activation analysis would seem to be especially suited to this type of sample. However, some restrictions might be found necessary for the irradiation of very volatile liquids or explosive compounds in a nuclear reactor.

G. Incinerator Particulates

The characteristics of this type of sample would probably be somewhere between fly ash and coal. No particular problems are foreseen that were not already mentioned, but no publications are available which specifically treat this material.

H. Slurry Streams, Feeds to/from Flotation Processes, and Sediments in Flotation Processes

These sample types are grouped together because there is so little published information on their analysis by nuclear methods. The only references that could be found were two papers, one previously mentioned under ores and minerals (96), plus one additional paper on the use of isotopic neutron sources for process control in the metallurgical industry (103).

Again, most of the sample types included here would appear to be very suitable to at least one of the activation analysis methods.

4. RESULTS AND DISCUSSION

The results of this survey of the analysis of environmental materials by nuclear methods are found in Table 1. Each element is listed along with pertinent information concerning its determination. As discussed in the introduction, no further breakdown of the data by sample type will be made; general comments can be found in Section 3 of this chapter.

In explanation of Table 1, each column will be commented upon here. For the second, third and fourth columns, (TECHNIQUE USED, ACTIVATION EQUIPMENT, and DETECTION EQUIPMENT, respectively) the definitions can be found at the bottom of the table, and are discussed here and elsewhere.

The instrumentation required for most of the activation procedures listed in Table 1 are first, an irradiation source (for AS and NAA, usually a high flux nuclear reactor) or access to one, and second, a pulse height analyzer and high resolution lithium-drifted germanium detector system for detecting and quantifying the induced radioactivities resulting from the irradiation. The activation analysis technique has the substantial advantage over most other trace analytical techniques in that after the sample has been irradiated (i.e., the trace element of interest has been made radioactive) normal contamination problems no longer exist. In fact, when radiochemical separations are used usually macro quantities (10-20 mg) of the element of interest are added to the sample as carrier to minimize separation and adsorption problems. Thus, to retain this advantage, handling and manipulation of the sample before irradiation, (preconcentration, dissolution, etc.) should be kept to a minimum.

Column 5, PREPARATION TIME, is an estimate of the time required for preparation of a sample for analysis. This time does not include the time necessary for counting a sample or calculation of the results, nor does it include the time required for dissolving the sample or for a chemical separation, should that be required. However, such factors are considered in estimating the cost of an analysis.

Column 6 contains the estimated DETECTION LIMIT, in micrograms. Most of the values for AS and NAA have been obtained from published compilations of experimental sensitivity values (104,105). In all cases the value quoted is for the "interference free" situation, using irradiation time of a few hours at a thermal neutron flux of $5 \times 10^{13} n.cm^{-2} sec^{-1}$. Where necessary, corrections have been made for counting with a Ge(Li) detector system. These detection limits are realistic, however, especially when employing an effective radiochemical separation to remove any interfering radioactivities from the sample. In fact, the listed detection limit can often be exceeded when specialized counting equipment is used. For instance, even though the listed detection limit for sodium in Table 1 is 10^{-3} μg, as little as 4×10^{-6} μg of sodium has been determined with a precision of better than ±10 percent, using a β-γ-γ sum-coincidence spectrometer (36,101).

In column 7, the estimated SAMPLE SIZE (grams) has been listed. This sample size is very flexible for neutron activation analysis and photon activation analysis, although less so for the other nuclear techniques. Samples have been analyzed which range from a few micrograms to tens of grams. However, general sampling considerations limit the sample size to more than 10 mg, while potential self-shielding effects usually limit the sample size to a gram or less.

In column 8, the MANPOWER SKILL LEVEL is assumed to be that of a skilled technician for the AS determinations. This has been shown to be true in a number of laboratories, providing the assumption in the next column is true, that an established analytical procedure is available. To provide that procedure, usually a scientist is required. Also, in many cases where a technician is indicated, a chemist will often be necessary if a radiochemical separation is required. In the table, a chemist is listed whenever special procedures are indicated.

In column 9, the COST PER ANALYSIS is estimated on the basis that an established analytical procedure is available, and that at least 100 samples are to be analyzed. Thus, the values given are for routine analyses, rather than special research type analyses.

In column 10, the SELECTIVITY has been evaluated on the basis of ease of determination by the primary nuclear analytical method. In the case of AS, this is a function of the gamma-ray energy, the half-life, and the general ability of the technique to successfully determine the element non-destructively in a variety of sample types. If a rapid and simple radiochemical separation would be very effective, this may also have been taken into consideration.

Column 11, COMMENTS, includes the evaluation of half-life, decay time, and/or radiochemical separations on sensitivity and specificity, and also lists the alternate nuclear method(s) of analysis for that element along with the pertinent reference(s).

Table 2 contains a listing of references for each individual element in a variety of matrices, often by a number of different nuclear methods. No attempt has been made to be exhaustive, but rather the aim has been to illustrate the analytical determination of that specific element.

No report on an analytical technique would be complete without a few comments on the potential errors and biases involved. These areas have been discussed extensively in the literature and so will not be further discussed here (106,107,108). It is sufficient to say that the uncertainties involved are well understood, so that with these techniques levels of accuracy and precision of ±5 percent are possible in many cases, and ±25 percent in almost all cases, in capable laboratories.

In conclusion, the various nuclear techniques of analysis have been shown to be capable of the determination of the elements listed in many sample matrices. These techniques, especially neutron activation analysis, activation spectrometry, and photon activation analysis, should be very useful in the analysis of trace elements in environmental samples.

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Table 1. Trace Elements in Environmental Materials

Element Determined	Tech. Used[a]	Activation Equip.[b]	Detection Equip.[c]	Prep'n Time	Detection Limit(μg)[d]	Sample Size(g)	Manpower Skill Level[e]	Cost Per Analysis[f]	Selectivity (Non-dest.)	Comments[g]
Mercury	AS	REACT	PHA-Ge	15 m	10^{-3}	.01-1.0	TECH	$50-100	Good	Chem. Sepn.++; Also: IDA (9)
Beryllium	CPAA	TVDG	PHA-NaI	30 m	1	<0.1	CHEM	100-200	Poor	Also: Photoneutron Tech(20,23,70); AS (48)
Cadmium	AS	REACT	PHA-Ge	15 m	10^{-2}	.01-1.0	TECH	50-100	Good	Often requires Chem. Sepn.; Also:FNAA (29)
Arsenic	AS	REACT	PHA-Ge	15 m	10^{-3}	.01-1.0	TECH	50-100	V. Good	Chem. Sepn.+
Vanadium	AS	REACT	PHA-Ge	15 m	10^{-3}	.01-1.0	TECH	50-100	V. Good	Short half-life
Manganese	AS	REACT	PHA-Ge	15 m	10^{-5}	.01-1.0	TECH	50-100	Exc.	
Nickel	AS	REACT	PHA-Ge	15 m	10^{-3}	.01-1.0	TECH	50-100	Good	Chem. Sepn.++
Antimony	AS	REACT	PHA-Ge	15 m	10^{-4}	.01-1.0	TECH	50-100	V. Good	Also: IDA (7)
Chromium	AS	REACT	PHA-Ge	15 m	10^{-2}	.01-1.0	TECH	50-100	Good	Often requires long decay time or Chem. Sepn.
Zinc	AS	REACT	PHA-Ge	15 m	10^{-2}	.01-1.0	TECH	50-100	V. Good	Either of two isotopes can be used; Also: IDA (9)
Copper	AS	REACT	PHA-Ge	15 m	10^{-3}	.01-1.0	TECH	50-100	Good	Chem. Sepn. ++; Also: IDA (8,13)
Lead	PAA	LINAC	PHA-Ge	30 m	5	.01-1.0	TECH	100-200	Good	Chem. Sepn. ++; Also: AS (48)
Selenium	AS	REACT	PHA-Ge	15 m	10^{-2}	.01-1.0	TECH	50-100	Good	Often requires long decay time
Boron	NTT	REACT	SPEC	30 m	10^{-1}	.001-.1	TECH	100-300	--	Also: AS (48); CPAA (24)
Fluorine	AS	REACT	PHA-Ge	15 m	10^{-2}	.01-1.0	TECH	50-100	V Good	Short half-life; Also CPAA (24); PAA (33)
Lithium	AS	REACT	SPEC	30 m	10^{-3}	.01-1.0	CHEM	100-300	Fair	V. short half-life, uses reactor pulse; Also: Secondary nuclear reaction (64)
Silver	AS	REACT	PHA-Ge	15 m	10^{-3}	.01-1.0	TECH	50-100	Good	Can also use very short half-life isotope (2)
Tin	AS	REACT	PHA-Ge	15 m	10^{-2}	.01-1.0	TECH	50-100	Fair	Requires long decay or Chem. Sepn.
Iron	AS	REACT	PHA-Ge	15 m	1	.01-1.0	TECH	50-100	V. Good	
Strontium	NAA	REACT	PHA-Ge	30 m	10^{-1}	.01-1.0	CHEM	100-200	--	Requires Chem. Sepn.; Also CPAA (41)
Sodium	AS	REACT	PHA-Ge	15 m	10^{-3}	.01-1.0	TECH	50-100	Exc.	
Potassium	AS	REACT	PHA-Ge	15 m	10^{-3}	.01-1.0	TECH	50-100	V. Good	
Calcium	AS	REACT	PHA-Ge	15 m	10^{-1}	.01-1.0	TECH	50-100	Exc	Short half-life; Also: CPAA (39)
Silicon	NAA	REACT	PHA-Ge	30 m	1	.01-1.0	CHEM	100-200	--	Requires Chem.Sepn.; Also: FNAA (53)
Magnesium	AS	REACT	PHA-Ge	15 m	1	.01-1.0	TECH	50-100	Good	Short half-life; Also: FNAA (29)
Uranium	AS	REACT	PHA-Ge	15 m	10^{-2}	.01-1.0	TECH	50-100	Good	Chem.Sepn.++; Also: NTT (34); Delayed neutron (50)
Thorium	AS	REACT	PHA-Ge	15 m	10^{-2}	.01-1.0	TECH	50-100	Good	Also: Delayed neutron counting (50)

[a] AS = Activation spectrometry (Instrumental neutron activation analysis); NAA = Neutron activation analysis; FNAA = Fast neutron activation analysis; CPAA = Charged particle activation analysis; PAA - Photon activation analysis; NTT = Nuclear track technique; IDA = Isotope dilution analysis

[b] REACT = Nuclear reactor; TVDG = Tandem Van de Graaf accelerator; LINAC = Linear electron accelerator

[c] PHA Ge = Pulse height analyzer with high resolution germanium gamma-ray detector; PHA-NaI = PHA with sodium iodide detector; SPEC = Special counting techniques (see references).

[d] Detection limits are micrograms of the element, for the interference-free situation; see text.

[e] TECH = skilled technician; CHEM = trained analytical chemist

[f] Estimated on the basis of large (>100) numbers of samples, using an established analytical procedure.

[g] CHEM SEPN + = Significantly improved determination with simple chemical separation; CHEM SEPN ++ = greatly improved determination with simple chemical separation; for explanation of other techniques used, see a.

Table 2
Element Index to References
Nuclear Methods

Element	References
Mercury	9,16,47,67,68,69,81
Beryllium	20,22,23,24,48,70
Cadmium	17,26,29,67,71
Arsenic	29,30,57,67,75,76,81
Vanadium	29,46,57,58,80
Manganese	3,14,29,65,76
Nickel	31,45,77,81
Antimony	7,28,29,76,81
Chromium	15,27,29,32,59,66,77,81
Zinc	9,14,27,29,32,60,61,65,67,76,77,81
Copper	8,13,14,18,27,29,62,65,76,77
Lead	42,48
Selenium	44,63,67,81,82
Boron	24,34,48
Fluorine	24,33,48
Lithium	38,48,64,74
Silver	1,2,29,37,77,83,84
Tin	29,30,56,81
Iron	10,14,40,66,76,77,81
Strontium	29,41,54,55
Sodium	19,29,36,65
Potassium	25,27,29,85
Calcium	6,29,39
Silicon	52,53,77,78
Magnesium	29,43,78
Uranium	4,5,25,34,35,50,51,74,79,81
Thorium	25,49,50,72,73,74

REFERENCES

1. Adam, F.; Hoste, J.; Speecke, A., Detection of Silver in Lead by Neutron Activation Analysis, Talanta 10, 1243 (1963).

2. Nakai, T.; Yajima, S.; Okada, M., Activation Analysis by Short-Lived Nuclides. IV. Determination of Silver by Silver-110, Nippon Kagaku Zasshi 81, 1422 (1960).

3. Bouten, P., Hoste, J., "Activation Analysis of Manganese in Cast Iron and High-Alloy Steels, Talanta 8, 322 (1961).

4. Decat, D., Van Zanten, H., Determination of Trace Quantities of Uranium by Neutron Activation Analysis, Anal. Chem. 35, 845 (1963).

5. Smales, A. A., Mapper, D., The Determination of Uranium in Fairly Pure Beryllium Metal by Neutron Activation and Gamma Spectrometry, Anal. Chim. Acta 125, 587 (1961).

6. Atchison, G. J., Beamer, W. H., Determination of Trace Impurities in Magnesium by Activation Analysis, Anal. Chem. 24, 1812 (1952).

7. Tejam, B. M., Haldar, B. C., N-Benzoyl-N-Phynylhydroxylamine as a Substoichiometric Extractant in Activation Analysis, IV. Determination of Antimony, Radiochem. Radioanal. Lett. 9, 189 (1972).

8. Miloslov, Krivanek, Frantisek, K., Substoichiometric Determination of Copper in High-Purity Metals by Activation Analysis, Talanta 12, 721 (1965).

9. Stary, J., Ruzicka, J., Isotope-Dilution Analysis by Solvent Extraction, II. Highly Selective Determination of Zinc with Dithizone, Talanta 8, 296 (1961).

10. Ibid, A New Principle of Activation Analysis Separations, 10, 287 (1963).

11. Trascenko, S. M., Extraction Radiometric Determination of Microgram Amounts of Lead by Isotope Dilution, "Radiometric Methods of Determ. of Microelem.," p. 93 Nauka, Moscow-Leningrad, 1965.

12. Carmichael, I. A., Whitley, J. E., Determination of Fluoride by Substoichiometric Isotope Dilution, Analyst 95, 393 (1970).

13. Ruzicka, J. Stary, J. Isotope Dilution Analysis by Solvent Extraction - IV, Selective Determination of Traces of Copper with Dithizone, Talanta 9, 617 (1962).

14. Brooksbank, W. A., Leddicotte, G., Neutron Activation Analysis of Aluminum-Base Alloys, Anal. Chem. 30, 1785 (1958).

15. Fasalo, G. B., Malvano, R., Solvent Extraction of Cr^{+6} with Tribenzylamine, Anal. Chim. Acta 29, 569 (1963).

16. Westermark, T., Activation Analysis of Mercury, Intern. J. Appl. Radiation Isotopes 9, 11 (1960).

17. Ricci, E., Mackintosh, W. D., Neutron Activation Method for the Determination of Traces of Cadmium in Aluminum, Anal. Chem. 33, 230 (1961).

18. Chinaglia, B., The Determination of Some Elements in Aluminum by Non-Destructive Radioactivation Analysis, Energia Nucl. 8, 571 (1961).

19. Plumb, R. C., Measuring Trace Elements, Nucleonics 14, 48 (1956).

20. Levine, C. A., Surls, J. P., Rapid, Nondestructive Determination of Beryllium Using Van de Graff X-Rays, Anal. Chem. 34, 1614 (1962).

21. Aidankin, B. C., etc., A Method for Beryllium in Ores by Means of Photoneutrons, AEC-TR-4498, 99-105 (1961).

22. Mezhiborskaya, K. B., Radioactivation Determination of Beryllium, Atomic Energy, USSR 6, 416 (1959).

23. Guinn, V. P., Lukens, H. R., The Photoneutron Determination of Beryllium and Deuterium, Trans. Amer. Nucl. Soc. 9, 106 (1966).

24. Ricci,E., Hahn, R. L., Sensitivities for Activation Analysis of 15 Light Elements with 18 MeV Helium-3 Particles, Anal. Chem. 39, 794 (1967).

25. Aruscavage, P. J., Millard, H. T., A Neutron Activation Analysis Procedure for the Determination of Uranium, Thorium and Potassium in Geologic Samples, J. Radioanal. Chem. 11, 67 (1972).

26. Lieberman, K. W., Kramer, H. H., Cadmium Determination in Biological Tissue by Neutron Activation Analysis," Anal. Chem. 42, 266 (1970).

27. Vasiler, I. Y., Razumana, G. N., Determination of Trace Impurities in Indium Antimonide by a Neutron Activation Method, Radiokhimiya 11, 573 (1969).

28. Adams, F., Hoste, J., Activation Analysis of Antimony by Sum-Coincidence Spectrometry, Nucleonics 22, 55 (1964).

29. LaFleur, P. D., and Becker, D. A., Editors, Activation Analysis Section: Summary of Activities, July 1969 to June, 1970, NBS Tech. Note 548 (1970).

30. Neirincka, R., Adams, F., Hoste, J., Determination of Impurities in Ti and Ti Dioxide by Neutron Activation Analysis. I. Simultaneous Determination of 16 Trace Elements, Anal. Chim. Acta 46, 165 (1969).

31. Neeb, K. A., Martin, J., Activation Analysis of Small Quantities of Tellurium, Chlorine, Thallium and Nickel in Selenium, Z. Anal. Chem. 247 (1962).

32. Ballaux, C., Dams, R., Hoste, J., Neutron Activation Analysis of High-Purity Selenium. Part V. Simultaneous Determination of Metallic Impurities, Anal. Chim. Acta 35, 141 (1966).

33. Wilkniss, P. E., The Determination of F, Cl, Br, and I in a Single Sample by Photon Activation Analysis, Radiochim. Acta. 11, 138 (June 1969).

34. Carpenter, B. S., Determination of Trace Concentrations of Boron and Uranium in Glass by the Nuclear Track Technique, Anal. Chem. 44, 600 (1972).

35. Becker, D. A., LaFleur, P. D., Determination of Trace Quantities of Uranium in Biological Materials by Neutron Activation Analysis Using a Rapid Radiochemical Separation, Anal. Chem. 44, 1508 (1972).

36. Becker, D. A., Neutron Activation Analysis of Sodium at the Picogram Level, Trans. Amer. Nucl. Soc. 12 495 (1969).

37. Morris, D. F. C., Killick, R. A., Determination of Silver and Thallium in Rocks by Neutron Activation Analysis, Talanta 4, 51 (1960)

38. Wiernik, M., Amiel, S., Activation Analysis of Lithium by Means of ^{8}Li and a Cerenkov Detector, IA-1190, 115-16 (1969).

39. Pretorius, R., Schweikert, E. A., A Method for Determining Calcium by Alpha Activation Analysis, SUNI-10, 19-20 (1969).

40. Mantel, M., Alhu, Yaron, Amiel, S, Trace Element Analysis of Standard Reference Materials, IA-1190, 118-19 (1969).

41. Debrun, J. L., Albert, P., Irradiation of Some Natural Elements by 35 MeV Photons. Application in Activation Analysis, Bull. Soc. Chim. Fr. 3, 1020 (1969).

42. Lutz, G. J., Determination of Lead in Environmental Samples by Photon Activation Analysis, Proc., Conf. on Nucl. Methods in Environ. Res. 144-49, ANS, Columbia, Mo. (1971).

43. Smathers, J. B., Duffey, D., Derivative Neutron Activation Determination of Magnesium, Nucl. Appl. Technol. 7, 84 (1969).

44. Nadkarni, R. A., Haldar, B. C., Substoichiometric Determination of Selenium by Neutron Activation Analysis, Radiochem. Radioanal. Letters 7, 305 (1971).

45. Ibid, Substiochiometric Determination of Nickel in Steel by Neutron Activation Analysis, 339 (1971).

46. Linstedt, K. D. and Kruger, P., Determination of Vanadium in Natural Waters by Neutron Activation Analysis, Anal. Chem. 42, 113 (1970).

47. Gillette, R. K., Investigations into the Determination of Mercury in Copper, Mound Laboratory Report No. MLM-1772 (TID-4500), Monsanto Research Corp. (1970).

48. Lukens, H. R., A Neutron Activation Analysis Method for the Determination of Be, Li, B, F and Pb. J. Radioanal. Chem. 1, 349 (1968).

49. Smith, G. W., and Mongan, D. M., The Determination of Thorium in Cerium Matrices by Neutron Irradiation: Use of Argonne Pneumatic Facility, Int. J. Appl. Rad. Iso. 16, 81 (1965).

50. Amiel, S. Analytical Applications of Delayed Neutron Emission in Fissionable Elements, Anal. Chem. 34, 1683 (1962).

51. Campbell, F. T. and Steele, E. L., Uranium Assay by Nondestructive Neutron Activation Analysis, Radiochem. Radioanal. Letters 11, 245 (1972).

52. Nadkarni, R. A., and Haldar, B. C., Determination of Silicon, Phosphorus and Sulfur in Alloy Steel by Neutron Activation Analysis, Anal. Chim. Acta 42 279 (1968).

53. Vogt, J. R. and Ehmann, W. D., Silicon Abundances in Stony Meteorites by Fast Neutron Activation Analysis, Geochim. Cosmochim. Acta 29, 373 (1965).

54. Higuchi, H., et al., Simultaneous Determination of Strontium and Barium by Neutron Activation Analysis with a Ge(Li) Detector, Anal. Chim Acta 44, 431 (1969).

55. Qureshi, I. H., and Meinke, W. W., Radiochemical Separation of Strontium by Amalgam Exchange, Talanta 10 737 (1963).

56. Hamaguchi, H., et al., Determination of Trace Quantities of Tin by Neutron Activation Analysis, Anal. Chim. Acta 30, 335 (1964).

57. Fukai, R., and Meinke, W. W., Activation Analysis of Vanadium, Arsenic, Molybdenum, Tungsten, Rhenium, and Gold in Marine Organisms, Limnology and Oceanography 7, 186 (1962).

58. Das, H. A., et al., Routine Determination of Vanadium in Silicate Rocks by Neutron Activation Analysis, Radiochem. Radioanal. Letters 4, 307 (1970).

59. Brunfelt, A. O., and Steinnes, E., Determination of Chromium in Rocks by Neutron Activation and Anion Exchange, Anal. Chem. 39, 833 (1967).

60. Ball, T. K., and Filby, R. H., The Zinc Contents of Some Geochemical Standards by Neutron Activation and X-ray Fluorescence Analysis, Geochim. Cosmochim. Acta 29, 737 (1965).

61. Bakes, J. M., and Jeffery, P. G., Determination of Zinc in Ores and Mill Products by Neutron Activation Analysis, Anal. Chem. 36, 1594 (1964).

62. Grimanis, A. P., Rapid Determination of Copper in Plants by Neutron Activation Analysis, Talanta 15, 279 (1968).

63. LaFleur, P. D., "Activation Analysis Section: Summary of Activities, July 1968 to June 1969," NBS Tech. Note 508 (1970).

64. Smith, G. W., et al., The Neutron Activation Determination of Lithium in the Presence of Alkali Metals and Magnesium, Anal. Chim. Acta 33, 1 (1965).

65. Becker, D. A., and LaFleur, P. D., Neutron Activation Analysis: Application of Trace Elements Analysis of Biological and Environmental Materials, "Proceedings, Fifth Ann. Conf. on Trace Substances in Environmental Health," Univ. of Mo., Columbia, Mo. 447 (1971).

66. Benson, P. A., and Gliet, C. E., Neutron Activation and Radiochemical Determination of the Molybdenum, Chromium, and Iron Content of Individual Stainless Steel Microspheres, Anal. Chem. 35, 1029 (1963).

67. Orvini, E., Gills, T., LaFleur, P., Nuclear Activation Analysis of Se, As, Zn, Cd, and Hg in Environmental Matrices, Trans. Amer. Nucl. Soc. 15, 642 (1972).

68. Rook, H. L., LaFleur, P. D., and Gills, T. E., Mercury in Coal: A New Standard Reference Material, Environmental Letters 2, 195 (1972).

69. Kennedy, E. J., et al., Environmental Studies of Mercury and Other Elements in Coal and Lake Sediments as Determined by Neutron Activation Analysis, "Proc. Conf. on Nuclear Methods in Environ. Research," ANS, 205, Columbia, Mo. (1971).

70. Mezhiborskaya, K. B., A Radioactivation Method for the Determination of Beryllium in Minerals, Raw Materials and in Hydrometallurgical Products, J. Anal. Chem. USSR 15, 323 (1960).

71. Bilefield, L. I., Determination of Cadmium in Rocks by Neutron Activation Analysis, Analyst 86, 386 (1961).

72. Leddicotte, G. W., Mahlman, H. A., Determination of Microgram and Submicrogram Quantities of Thorium by Neutron Activation Analysis, "Intern. Conf. Peaceful Uses of At. Energy," 8, 250 (1955).

73. Mantel, M., Propai, S. T., Amiel, S., Neutron Activation Analysis of Thorium in Rocks and Ores by Multiple Gamma Ray Peak Ratio Determination, Anal. Chem. 42, 267 (1970).

74. Amiel, S., New Methods of Radio-Activation Analysis Based on Delayed Neutron Emission and Secondary Reactions, "Utilization of Research Reactors," Vol. 3, 307-14, Vienna IAEC, London (1962).

75. Saskoloka, H., Rowinska, L. The Search for Internal Isotopic Tracers in Metallurgical Materials. I. Determination of In, W, As, Au, Sc, Re, Ir, and Ca by the Neutron Activation Method, J. Radioanal. Chem. 7 29 (1971).

76. Lamb, J. F., et al., Application of Lithium-Drifted Germanium Gamma-Ray Detectors to Neutron Activation Analysis. Non-Destructive Analysis of a Sulfide Ore. Anal. Chem. 38, 813 (1966).

77. Leddicotte, G. W. et al., The Determination of Trace Elements in Reactor Materials by the Method of Neutron Activation Analysis, TID-7555, 192-215 (1958).

78. Lobanov, E. M., Mingalier, G. G., Rapid Neutron Activation Determination of Si, Al, Ba and Mn in Synthetic Micas, Aktivatsionnyii Analiz Elementiogo Sastava Geologicheskikh Obekter, 77-83, Tashkent (1967).

79. DeLange, P. W., et al., Critical Evaluation of Spiking of Low Grade Ore Samples in Activation Analysis for Gold and Uranium, Talanta 15, 1488 (1968).

80. Wahl, W. H., Molinski, V. J., Rapid Radiochemical Separation Procedures for Activation Analysis Indicators, "Proc., Inter. Conf. Modern Trends in Act. Anal." 44, College Station, Texas (1965).

81. Shah, K. R., Filby, R. H., Holler, W. A., Determination of Trace Elements in Petroleum by Neutron Activation Analysis. II. Determination of Sc, Cr, Fe, Co, Ni, Zn, As, Se, Sb, Eu, Au, Hg and U, J. Radioanal. Chem. 6, 413 (1970).

82. Pillay, K. K. S., Thomas, C. C., Neutron Activation Analysis of the Selenium Content of Fossil Fuels, Nucl. Appl. Technol. 7, 478-(1969).

83. Turkstra, J., Pretorius, P. J., Nondestructive Determination of Platinum Metals in Ores, Matte and Lead Assay Beads by Reactor Activation Analysis and High Resolution Gamma Spectrometry, Anal. Chem. 42, 835 (1970).

84. Morris, D. F. C., Killick, R. A., The Determination of Silver in Galena and Blende by Radioactivation Analysis, Anal. Chim. Acta. 20, 587 (1959).

85. Sorin, M., Popescn, G., Determination of Potassium in Geological Samples Using Neutron Activation Analysis, Ann. Soc. Geol. Belg. 94, 132 (1971).

86. Samsahl, K., Brune, D. and Wester, P. O., Simultaneous Determination of 30 Trace Elements in Cancerous and Non-Cancerous Human Tissue Samples by Neutron Activation Analysis, Internat. J. Appl. Rad. Isotopes 16, 273 (1965).

87. Nadkarni, R. E., and Ehmann, W. D., Determination of Trace Elements in Biological Standard Kale by Neutron Activation Analysis, J. Radioanal. Chem. 3, 175 (1969).

88. Colombo, U. P., et al., Systematic Neutron Activation Technique for the Determination of Trace Metals in Petroleum, Anal. Chem. 36, 802 (1964).

89. Guinn, V. P. and Bellanca, S. C., Neutron Activation Analysis Identification of the Source of Oil Pollution of Waterways, "Proceedings, 1968 Internat. Conf. Mod. Trends in Act. Anal.," NBS Spec. Publ. 312, Vol. I, p. 93 (1969).

90. Internat. Atomic Energy Agency, Uses of Activation Analysis in Studies of Mineral Element Metabolism in Man, Report of a Panel Meeting, Teheran, IAEA Report No. 122, Vienna (1970) (11 pages).

91. Internat. Atomic Energy Agency, "Nuclear Activation Techniques in the Life Sciences," Proceedings of a Symposium, Amsterdam, May 1967, IAEA, Vienna (1967).

92. DeVoe, J. R., Editor, "Modern Trends in Activation Analysis. Chapter 2. Biomedical Applications," Proceedings of the 1968 International Conference on Modern Trends in Activation Analysis, NBS Spec. Publ. 312, Vol. 1, p 98-212 (1969).

93. Ibid, "Chapter 4. Geochemical and Cosmochemical Applications," pp 288-413.

94. Brunfelt, A. O., and Steinnes, E., "Activation Analysis in Geochemistry and Cosmochemistry," Universitetsforloget, Oslo (1972).

95. Allen, R. O., et al., Neutron Activation Analysis for 39 Elements in Small or Precious Geologic Samples, J. Radioanal. Chem. 6, 115 (1970).

96. Navalikhin, L. V., et al., Simultaneous Determination of Lead, Copper, and Zinc in Multimetal Ores and Their Processed Products by Activation Analysis, J. Radioanal. Chem. 11, 257 (1972).

97. Guinn, V. P., et al., The Trace Element Characterization of Crude Oils and Fuel Oils Via Instrumental Neutron Activation Analysis, "Proc., Nuclear Tech. in Environmental Pollution," Salzburg, p. 347, IAEA, Vienna (1971).

98. Malvano, R., Neutron Activation Analysis in Metallurgy, Atompraxis 11, 309 (1965).

99. Albert, P., Application of Radioelements to Investigating the Purification of Metals by the Zone Refining Method: Systematic Analysis After Irradiation with Neutrons (From the book "New Physical and Chemical Properties of Metals of Very High Purity," New York, Gordon and Beach Science Publishers) pp 1-51 (1965).

100. Bunshah, R. F., editor, "Modern Analytical Techniques for Metals and Alloys: Part 2," Interscience, New York (1970). (Above includes six chapters on activation analysis, including chapters on thermal neutron activation, fast neutron activation, and photon and charged particle activation.)

101. LaFleur, P. D., Editor,"Activation Analysis Section: Summary of Activities, July 1968 to June 1969." NBS Tech. Note 508, p 76 (1970).

102. DeVoe, J. R., Editor,"Radiochemical Analysis: Activation Analysis, Instrumentation, Radiation Techniques, and Radioisotope Techniques, July 1965 through June 1966," NBS Tech. Note 404, p 29 (1966).

103. Kuusi, J., The Application of Isotopic Neutron Sources to Chemical Analysis for Process Control in the Metallurgical Industry, "Proc., 1968 Internat. Conf. Mod. Trends Act. Anal.," NBS Spec. Publ. 312, Vol. I, p. 450 (1969).

104. Yule, H. P., Experimental Reactor Thermal-Neutron Activation Analysis Sensitivities, Anal. Chem. 37, 129 (1965).

105. Yule, H. P., Reactor Neutron Activation Analysis: Instrumental Sensitivities in Six Matrix Materials, Anal. Chem. 38, 818 (1966).

106. Smith, G. W., et al., Determination of Trace Elements in Standard Reference Materials by Neutron Activation Analysis, Anal. Chim. Acta. 38, 333 (1967).

107. DeVoe, J. R., Editor, "Proceedings, 1968 International Conf. Modern Trends in Activation Analysis, Chapter 15, Accuracy, Precision and Standards." NBS Spec. Publ. 312, Vol. II, (1969).

108. Cook, G. B., et al., International Comparison of Analytical Methods for Nuclear Materials - I, Talanta 10, 917 (1963).

CHAPTER 3

SPARK SOURCE MASS SPECTROMETRY

Paul J. Paulsen

1. INTRODUCTION

In spark source mass spectrometric (SSMS) analysis, samples are introduced as solid "electrodes" into the source chamber which is evacuated to a pressure of 1×10^{-7} to 1×10^{-8} torr. Ions are produced from a pair of sample electrodes by imposing a pulsed radiofrequency voltage of 20 to 80 keV between them. The spark produced vaporizes and ionizes all elements in a small volume of the sample with each pulse. The high energy available in the spark results in the production of multiply charged as well as singly charged ions of all elements. The +1 ions, however, are the most abundant species with a decrease in abundance with each increasing charge (i.e. $Fe^{+1} > Fe^{+2} > Fe^{+3}$, etc.). The ions are accelerated by a 24 kV D.C. potential and pass through an electrostatic sector and then a magnetic sector. The ions are resolved into individual beams in the magnetic sector and dispersed according to their mass to charge ratio. A photographic plate at the exit of the magnet simultaneously detects all elements from Li (mass 7) to U (mass 238) on each exposure. By making a graded series of exposures covering 5 to 6 orders of magnitude, it is possible to determine elements present from the ppb level up to the 100 percent level.

Recently instruments have been produced which have electronic detection as well as photographic detection. These instruments use an ion multiplier to measure ion currents of a single mass line at a time. The full mass range is covered by scanning the ions of the individual lines sequentially across the ion multiplier (by changing the magnetic field strength).

Spark source mass spectrometry is ideally suited to survey an unknown sample for all possible elements from major constituents to those present at the ppb level. The spark source has no inherent "blind spots" for any element and detects all elements with approximately the same sensitivity. Under optimum conditions a detection limit of a few ppb can be obtained for all elements while consuming as little as 10 to 100 mg of sample. This high absolute sensitivity makes the technique applicable to both the analysis of low levels of concentration and the analysis of small samples (such as particulates from a low-volume air sample).

A. Interferences

Although the SSMS can potentially detect all elements, there will be interferences present which may hinder or prevent the analysis of some elements in real life samples. There are two main sources of possible interferences, the +2, +3, etc. multiply charged ions and molecular ions (hydrocarbons, metal dimers, oxides, etc.) having the same nominal mass to charge ratio as the singly charged line of the element being determined.

Control of experimental conditions and proper plate interpretation techniques minimize the number of potential interferences. An experienced SSMS operator is not likely to misidentify the interference as an element. The existence of actual interferences and the concentration level where the interference starts will depend on what other elements are present in the sample and their concentrations. The actual sample must be run to determine which elements have interferences (at what concentration levels), however from previous experience we know it will be only a small percentage of the possible elements. In a recent publication in American Laboratory, R. Brown [1] reported the simultaneous determination of from 40 to 60 elements in single samples by SSMS. The sample types ranged from lung tissue and coal dust to fly ash.

B. Sample Requirements

The spark source requires conducting or semiconducting samples for sparking which are stable under the 10^{-7} to 10^{-8} torr vacuums present in the instrument. Powders can be mixed with graphite or silver powder and compressed into electrodes suitable for analysis. Techniques are available to analyze essentially any form of sample from liquids to insulating solids by SSMS, however it is important to note that any sample manipulation will result in some degree of contamination of the sample when analyzing at the sub-ppm level for all possible elements.

The high absolute sensitivity of the spark source requires good sample homogeneity in order for the small volume of sample consumed in the analysis to be representative of the bulk of the sample. Powders used for analysis should be ∿100 mesh size and be well mixed in order to meet this homogeneity requirement.

C. Sensitivity

Modern spark source instruments can obtain 1 ppb detection limits with 1 hour of sample sparking at ∿2000 resolution ($\frac{\text{mass}}{\Delta\ \text{mass}}$) using photographic detection. If the instrument has electrical detection, 0.1 ppm detection limits are obtained when scanning the entire mass range in ∿10 minutes. Detection limits at the ppb level are obtained from electrical detection when using the peak switching mode (1 to 30 sec integration of each peak), however this mode only allows examination of a limited number of elements in each sample (10 to 20 elements). Both modes of electrical detection are normally operated at a resolution of only 500, making it incapable of resolving any interference involving a line having the same nominal mass as the analytical line being measured.

2. PRECISION OF MEASUREMENTS BY SSMS

The uniformity of the photographic plates used in SSMS analysis limits the precision of measurements to ∿±5 percent, and this level of precision is usually only obtained in the measurement of the isotopic ratios for an element, provided the ratio is measured within a single exposure. When measurements are made involving the absolute intensities between exposures, (as in most types of analysis) precisions of ±15 to 20 percent are usually obtained. The scanning mode of electronic detection given precisions of ±10 to 30 percent [2] and in the peak switch mode of electronic detection, precisions can approach ±1 percent [2] under favorable conditions.

3. ACCURACY OF ANALYSIS BY SSMS

The accuracy of a spark source analysis on the other hand will usually depend on the availability of a suitable reference standard with the same composition (same basic matrix). With a good reference standard the obtainable accuracies can equal the precision values just mentioned. The following is a general outline of different approaches to the standard's problem:

A. No Standards Used; Concentrations Estimated

It was mentioned previously that the SSMS detects all elements with approximately the same sensitivity. The accepted method of computing results for SSMS analysis when no standard is available is to assume that all elements have the same atomic sensitivity as the matrix and equate relative line intensities to element concentrations. Results calculated in this manner are usually reported to be within a factor of 3 to 10 of the correct result. A study at NBS of 12 Standard Reference Materials (all metals or metal alloys) by SSMS yielded analysis with 75 percent of the computed impurity concentrations within a factor of 3 and 95 percent within a factor of 5 of the certified concentrations.

Although this range in accuracy may not be adequate for the final analysis of a sample, the complete elemental coverage and the sub-ppm detection limits make it the ideal survey technique. An analysis of this type will provide the information necessary to make the decision as to which elements need to be determined more accurately by other techniques.

While an analysis without a standard can be in error by a factor of 3 to 10, it is possible to compare the relative concentrations of impurity elements in different samples to within ±20 percent, providing the basic matrix composition does not change. A significant number of useful SSMS analyses in the past have involved the detection and correlation of relative changes in concentration even though these changes were small compared to the uncertainty in the reported absolute concentration levels.

B. Analysis Using Standard Reference Materials (SRM's)

Many certified SRM's are available from NBS and other sources which can be used as reference standards for SSMS analysis. As long as the major components of the standard and the unknown samples are the same, a single standard is valid for a wide concentration range. (Halliday et al. [3] showed a linear response for gold through five orders of magnitude in a titanium matrix.)

Use of a standard, and careful control of all instrument parameters produce ±15 percent accuracy with the photographic plate detection; ±6 to 8 percent accuracy has been obtained under special conditions [4]. Electrical detection in the scanning mode can yield ±10 to 30 percent accuracy [2] depending on the number of scans, and peak switching ±4 to 7 percent [2,5]. At the lower error levels and low concentrations the uncertainties in the certified standard may be a significant source of error.

Unfortunately, most standards will have only 20 to 30 elements certified, these may cover only half of the elements detected in a survey analysis and thus still present a problem.

C. Analysis Using Synthetic Standards

Powdered samples which are normally mixed with graphite (silver, etc.) powder and pressed into electrodes for analysis, and other types of samples can be conveniently compared to synthetic standards prepared in an identical manner. Griffith et al. [6] used this method for determination of rare earths in rare earth oxides, and Nicholls et al. [7] used it for determining elements in geological materials. Accuracies from ±20 to ±5 percent are claimed using photoplate detection. The accuracy of analysis will depend upon the synthetic standard having elements chemically combined in the same way as they are in the sample. Thus, $CrCl_3$ (or $K_2Cr_2O_7$) added to a graphite mix in a known concentration could not serve as a reference standard for the determination of Cr in a ruby powder (mixed with graphite) where the Cr is locked inside the highly refractory Al_2O_3 matrix. It could serve quite adequately, however, for determining Cr in water solutions which were prepared for sparking by evaporation with graphite powder, mixing, and pressing into electrodes.

D. Analysis Using Stable Isotope Dilution

Isotope dilution analysis with the SSMS can provide an absolute method of analysis (requiring no standards) to accuracies of ±5 percent for any element having two or more stable isotopes. With this technique a known amount of an enriched separated isotope (spike) of an element is added to the sample being analyzed; following chemical and physical equilibrium of the "spike" isotope with the natural isotopes of the element, the element is separated from the matrix and the altered isotopic ratio is determined with the SSMS. Only three measured quantities are required to compute a concentration: (1) the sample weight, (2) the amount of separated isotope added and (3) the altered isotopic ratio. In most samples several elements can be determined simultaneously by SSMS isotope dilution, from a single sample treatment. This is the only technique used at NBS for the SSMS analysis of Standard Reference Materials for certification. Elemental concentrations have ranged down to the low ppb level [8,9,10], and to sub-ppb levels [11] for systems amenable to preconcentration.

In all SSMS analysis techniques, other than isotope dilution, the accuracy of an analysis ultimately depends on the ability to run both the sample and reference standard under identical conditions. The sample homogeneity, the gap between sample electrodes during sparking, their alignment with the ion optical axis of the instrument, the voltage of the R.F. spark, plus other operational parameters can affect the absolute intensity of an element line when compared to the total ion current or the intensity of an internal standard element. Although these parameters affect the absolute intensity of an element's lines, they have no measurable effect on the isotope ratio of an element (photographic detection) measured on a single exposure. The precision and accuracy of an analysis by SSMS isotope dilution is therefore limited only by the ±5 percent uniformity of the photographic plate.

4. PROCEDURE FOR ANALYSIS OF MATERIALS

The materials covered by this report can be grouped according to the treatment required to get the samples into forms suitable for sparking in the mass spectrometer. The forms used will, in turn, be controlled by the standardization method (precision and accuracy) desired.

Group I

Coal, oil, organometallics (organic content)

Group II

Fly ash, ores, minerals, incinerator particles, slurry streams, feeds to and from flotation processes, sediments in flotation processes (all inorganic solids [after evaporation of water], nonconducting)

Group III

Metals, alloys (conducting samples which can be run as is, with no treatment other than cutting to size)

A. Group I Matrices

The SSMS has about the same sensitivity for organic compounds as it does for inorganic elements. The ∿2000 resolution normally obtained with photographic detection will completely resolve equal-intensity hydrocarbon and element lines having the same nominal mass. In the presence of a gross excess of hydrocarbons from Group I samples, however, higher resolution would be required to maintain separation of the lines. SSMS instruments now being sold can be adjusted to resolutions of 10,000 and higher, but at the expense of sensitivity. The 500 resolution of the electronic detection mode is incapable of resolving hydrocarbons from elements at the same nominal mass and cannot be used when hydrocarbon lines are present. Coal is presently being run directly [1,12] and after dry ashing. Dry ashing not only permits the use of the higher sensitivity 2000 resolution range, it also preconcentrates the inorganic material being analyzed from 10 to 100-fold. Dry ashing can lose volatile elements such as Hg, Te, Cd, As, etc. If analysis of such elements is desired, a wet ash procedure would be better. Both oils and organometallics can be handled by wet ashing, possibly in sealed tubes or bombs.

B. Group II Matrices

The slurry streams, feeds to and from flotation processes, and sediments in flotation processes require removal of water by drying. In the dry form all of this group could be handled the same way. Direct sparking of these nonconducting materials require mixing with a conducting powder such as graphite (silver, etc.). Sample grinding may be necessary to obtain the ∿100 mesh size required for sample homogeneity. Geological Survey samples could be used as reference standards for some minerals, ores, and materials from the flotation process but certainly not for all of them and not for either fly ash or slurry streams. A synthetic standard mixed with graphite would certainly give better results than estimating concentrations, but the fact that the synthetic standard does not match the physical-chemical form of the actual samples could cause relatively large errors. The problem of producing a synthetic standard identical to a sample could be solved by dissolving all samples in mineral acids (this also applies to Groups I and III). Such solutions could then be exactly duplicated with a synthetic mixture.

C. Group III Matrices (metals and alloys)

No special sample treatment is normally required. Standard Reference Materials are most readily available for these type samples. If a standard is not available or if critical elements have not been certified in the SRM's, the sample can either be dissolved for a comparison to a synthetic standard or analyzed by isotope dilution.

It has been pointed out that to obtain a synthetic standard that is identical to a sample, the sample itself may have to be dissolved. Any such sample processing will introduce contamination of the samples. Dissolution of samples (wet ashing) would normally be done with excess amounts of acids. The problems actually encountered will depend on what elements are to be determined and their concentration levels with respect to the purity and amounts of acids being used for dissolution. In addition, dissolution dilutes the sample and hence reduces sensitivity. However, even if the subsequent processing involves redrying of the sample, the added acid anions still represent a significant amount of sample dilution. The added anions are even more troublesome as a source of molecular interference when combined with cations. The alkalis and alkaline earths are particularly inclined to combine with anions to form ionized molecular species in the spark source.

Samples starting as water solutions or samples dissolved for purpose of analysis can be handled a number of ways:

1. They can be frozen in a liquid nitrogen cooled "cup" and sparked directly using a high purity counter electrode [13].

2. They can be evaporated to dryness on a high purity substrate and sparked against a high purity counter electrode [14].

3. The solution can be slurried with graphite, evaporated to dryness, mixed, and pressed into electrodes [1].

4. The solution can be "spiked" and analyzed by isotope dilution analysis.

System 3 would be most amenable for use with the "synthetic" reference standard.

5. ANALYSIS BY ISOTOPE DILUTION

Isotope dilution is the most accurate means of analysis available to the SSMS. However, it does not have the element coverage that is available in the direct sparking of a sample. Factors involved in isotope dilution analysis by SSMS are:

1. It applies only to elements with two or more isotopes and cannot be used for gases.

2. The requirement of mixing the spike isotope with the natural element isotopes physically and chemically (both in oxidation states and in chemical form) means that all samples must be put into solution as a minimum treatment.

3. Measurement of an isotope ratio by SSMS requires about 10^{-8} to 10^{-6} grams of an element for consumption in the sparked volume (<10 mg).

4. Item 3 plus problems of interferences in essence require a preconcentration step for any isotope dilution analysis of elements below a few hundred ppm. The preconcentration should include the removal of water, the major (unanalyzed) cations and anions. Since only the isotope ratio is measured for each element, the efficiency of a preconcentration procedure is not important so long as enough material is recovered to measure the ratio. General group separation procedures such as electrodeposition, anion or cation exchange and solvent extraction have been used in our laboratory for preconcentration. Generally the last step has been electrodeposition onto pure gold wires for sparking. Preconcentration of water and acids [11] is obtained simply by evaporation onto the gold wires used for sparking.

5. Analysis by isotope dilution requires that the measured altered ratio be significantly different from both the natural and "spike" isotopic ratios. A photoplate will give the best accuracy if the final ratio is ∿1 (2 if the natural ratio is 1).

6. Item 5 plus the limited dynamic range of intensity covered by a single exposure on a photoplate restricts the concentration range covered by a single spiking to a factor of ∿10 up or down from the optimum ratio.

7. Our laboratory has not attempted isotope dilution analysis on SRM's above several hundred ppm since other techniques are normally available at NBS which can give better accuracy than the SSMS at these high concentrations. For elements attempted below this concentration, a single group separation technique has enabled successful isotope dilution analysis of approximately <u>half</u> of the elements present in the sample. Six to eight elements are usually determined simultaneously in each sample.

There is a specific application of environmental interest where isotope dilution by SSMS can be both very effective and relatively inexpensive to use. It is the analysis problem of testing a material to see whether it meets certain legal <u>concentration specifications for trace elements</u> (e.g., pollution standards!!).

In this situation, the sample would be spiked with the exact amount of spike isotope that gives an altered isotope ratio of 1 at the critical specified concentration. A visual inspection of isotope ratios on the SSMS photoplate would rapidly identify any element that is present in an amount grossly above or below the specification levels. Only those elements whose concentrations are close to meeting or failing specifications would have to be measured with a densitometer. The analysis would give its most reliable results exactly at the critical, specified concentrations. If this technique were applied to the analysis of water supplies, evaporation-preconcentration techniques could give detection limits as low as 0.01 to 0.1 parts per billion on ∿50 ml of water [11].

6. ELEMENT COVERAGE OF SSMS ANALYSIS

All analyses by SSMS will involve the determination of many elements simultaneously from each sample. Since the only "blind" spots in SSMS analysis are generated by the constituents of the sample itself, the sample must be analyzed before it is known which elements cannot be determined. The total number of interferences will be always less than ∿30 percent of all the elements. Table 1 is taken from a recent publication by Brown et al. [1]. He was able to detect over 60 elements in both fly ash and coal samples by SSMS.

Table 1 lists all 27 of the desired elements detected in fly ash and 26 of the 27 desired elements found in coal. Overall, for group I, II, and III samples, we can estimate that at least 20 elements of the 27 listed for this report could be determined for each sample; however, the specific elements would not be known until the samples were run. In general, the low mass elements are the ones having most interferences.

Isotope dilution would have the lowest element coverage of any SSMS technique. The NBS laboratory has determined in various sample matrices, 16 of the 27 elements listed. (Hg, Cd, Ni, Sb, Cr, Zn, Cu, Pb, Se, Ag, Sn, Fe, Sr, K, Ca and Mg.) U and Th should also be readily determinable. Experience with NBS SRM samples indicates that about 10 to 12 of the elements can be separated as a group with a single separation procedure and be determined simultaneously by SSMS isotope dilution. One-gram samples would give analyses down to ∿0.1 ppm with accuracies of ±5 to 10 percent at 1 ppm and higher.

7. COST (TIME) OF ANALYSIS BY SSMS

It is assumed that the number of similar samples to be analyzed will be large enough so that the initial set up times can be ignored. These estimates are based on experiences of a one-man laboratory; larger laboratories should be more efficient. Only two examples will be given which represent extremes for cost, coverage and accuracy; (a) an all inclusive survey analysis with estimations of concentrations (factor of 3 to 10) and (b) isotope dilution analysis of a limited number of multi-isotope elements.

1. Survey analysis for all possible elements, no reference standard used, visual interpretation of photographic plate (no densitometry), all samples except possibly oil and organo-metallics.

   a. Sample preparation ∿1 hour or less.

   b. SSMS instrument and photoplate development ∿1 hour.

   c. Photoplate interpretation ∿1 hour.

   TOTAL Two to four samples tested for ∿60 elements per man day - results ±3 to 10 fold.

2. Isotope dilution analysis. Accurately spiked sample, densitometry of photographic plate, computer calculations of results for all samples.

   a. Sample dissolution, spiking, preconcentration ∿1/2 day.

   b. SSMS instrument time and plate development <1 hour.

   c. Densitometry of plate and computation of results ∿3 hours.

   TOTAL One sample for 8 to 12 elements per man day - results to ±5 to 10 percent accuracy.

8. CONCLUSION

There are two types of applications where the SSMS can be clearly superior to any other single analytical method.

1. To survey a completely "unknown" sample for all possible trace elements to concentrations well below 1 ppm. A direct sparking without standards (x3 to x10 accuracy) would give an analysis adequate for making decisions as to which elements were at high enough concentrations to require an accurate analysis. This SSMS survey analysis would also contain enough information to permit decisions to be made as to which analytical techniques should be used for each element, based on the concentration levels sought and possible interferences from other elements.

2. Use of SSMS isotope dilution to test environmental samples for compliance to preset standards of acceptable concentration levels for toxic elements (many elements simultaneously).

Such samples can be spiked so that each element being tested gives an altered isotope ratio of 1 (or 2 for some elements) at its critical level. In this case rapid visual plate interpretation would identify all elements which grossly pass or fail. Only elements near the critical concentrations would require the more precise densitometry data, and these results would be most reliable at the specified concentration. Easily preconcentrated samples, such as drinking water supplies, could have detection limits as low as 0.1 to 0.01 parts per billion from 50 ml samples.

Table 1

Simultaneous Determination of Twenty-seven Elements by Spark-Source Mass Spectrometry in Typical Coal and Fly Ash Samples[a]

Element	Matrix Coal(1) (ppm)	 Fly Ash(1) (ppm)
Hg	0.08	<0.01
Be	1.2	8.0
Cd	0.19	0.70
As	0.30	22
V	12	50
Mn	30	400
Ni	2.7	50
Sb	0.14	4.5
Cr	4.5	110
Zn	10	260
Cu	25	200
Pb	3.9	60
Se	0.32	0.30
B	42	230
F	5.7	150
Li	--	42
Ag	0.22	0.50
Sn	0.83	60
Fe	1600	Major
Sr	100	2000
Na	5000	Major
K	410	7000
Ca	4000	Major
Si	Major	Major
Mg	4500	Major
U	1.9	30
Th	4.5	40

(a) In addition to the above elements of interest, reference (1) lists values for 34-38 additional elements.

Table 2

Subject Index to References

I. Precision and/or Accuracy of SSMS Analysis
1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 13, 16, 17, 18, 23, 25, 26, 28, 32, 33, 34, 35, 36, 37, 38, 40, 41, 43, 51

II. Survey Analysis, Concentrations Estimated to Factor 3 to 10
1, 3, 12, 14, 18, 20, 21, 22, 23, 24, 25, 27, 29, 31, 39, 42, 45, 46, 49, 50, 53

III. Analysis Using Synthetic Reference Standard
6, 7, 17, 25, 26, 28, 32, 35, 36, 37, 38, 41, 48

IV. Analysis Using Certified Standard Reference Materials
2, 3, 4, 7, 8, 9, 10, 16, 18, 26, 32, 33, 34, 37, 40, 46, 47, 51, 52

V. Analysis Using Isotope Dilution SSMS
8, 9, 10, 11, 19, 43, 44

VI. Analysis of Solutions or Samples Dissolved for Analysis
1, 8, 9, 10, 11, 13, 14, 17, 19, 20, 21, 25, 27, 28, 30, 37, 38, 39, 42, 43, 44, 45, 49

VII. Group I Samples - Coal, Oil, Organometallics and High Organic Content Samples
1, 12, 17, 20, 22, 23, 24, 26, 28, 41, 43, 45, 53

VIII. Group II Samples - Fly Ash, Ores, Minerals, Slurry Streams, etc.
1, 7, 16, 17, 20, 22, 24, 32, 33, 34, 35, 36, 37, 40, 46, 47, 48, 50

IX. Group III Samples - Metals and Alloys
1, 2, 3, 4, 5, 6, 8, 9, 10, 18, 19, 26, 27, 31, 36, 37, 42, 52

X. Analysis Using Electronic Detection
1, 2, 5, 20, 22, 30, 31, 36, 37, 45, 49, 51, 52

References

[1] Brown, R., Jacobs, M. L., and Taylor, H. E., A Survey of the Most Recent Applications of Spark Source Mass Spectrometry, American Laboratory, 4, 29 (1972).

[2] Bingham, R. A. and Elliott, R. M., Accuracy of Analysis by Electrical Detection in Spark Source Mass Spectrometry, Anal. Chem., 43, 43 (1971).

[3] Halliday, J. S., Swift, P., Wolstenholme, W. A., "Quantitative Analysis by Spark Source Mass Spectrometry", Adv. in Mass Spectrom., 3, Int. Petrol. London, 143 (1966).

[4] Franzen, J. and Schuy, K. D., The Effect of Electrode Shape on Analytical Precision in Spark Source Mass Spectrometry, Int. Mass Spectrometry Conference, Berlin, 25-29 September 1967.

[5] Evans, C. A., Jr., Guidoboni, R. J., and Leipziger, F. D., Routine Analysis of Metals Using a Spark Source Mass Spectrograph with Electrical Detection, Appl. Spec., 24, 85 (1970).

[6] Griffith, D. A., Conzemius, R. J., and Svec, H. J., Determination of Rare Earths in Selected Rare Earth Matrices by Spark Source Mass Spectrometry, Talanta, 18, 665 (1971).

[7] Nicholls, G. D., Graham, A. L., Williams, E., and Wood, M., Precision and Accuracy in Trace Element Analysis of Geological Materials Using Solid Source Spark Mass Spectrography, Anal. Chem., 39, 584 (1967).

[8] Paulsen, P. J., Alvarez, R., and Kelleher, D. E., Determination of Trace Elements in Zinc by Isotope Dilution Spark Source Mass Spectrometry, Spectrochimica Acta, 24B, 535 (1969).

[9] Alvarez, R., Paulsen, P. J., and Kelleher, D. E., Simultaneous Determination of Trace Elements in Platinum by Isotope Dilution and Spark Source Mass Spectrometry, Anal. Chem., 41, 955 (1969).

[10] Paulsen, P. J., Alvarez, R., and Mueller, C. W., Spark Source Mass Spectrographic Analysis of Ingot Iron for Silver, Copper, Molybdenum, and Nickel by Isotope Dilution and for Cobalt by an Internal Standard Technique., Anal. Chem., 42, 673 (1970).

[11] Kuehner, E. C., Alvarez, R., Paulsen, P. J., and Murphy, T. J., Production and Analysis of Special High-Purity Acids Purified by Sub-Boiling Distillation, Anal. Chem., 44, 2050 (1972).

[12] Kessler, T., Sharkey, A. G., Jr., and Friedel, R. A., Spark-Source Mass Spectrometer Investigation of Coal Particles and Coal Ash, 19th Annual Conf. on Mass Spectrometry and Allied Topics, May 2-7, 1971, Atlanta, Georgia.

[13] Owens, E. B., Analysis of Frozen Aqueous Solutions by Spark Source Mass Spectroscopy, Anal. Letters, 3, 223 (1970).

[14] Ahearn, A. J., Mass Spectrographic Detection of Impurities in Liquids, J. Appl. Phys., 32, 1197 (1961).

[15] Blosser, E. R. and Thompson, R. J., Elemental Analysis of Air Particulates Using Spark Source Mass Spectrography, 19th Annual Conf. on Mass Spectrometry and Allied Topics, May 2-7, 1971, Atlanta, Georgia.

[16] Roaldset, E., Relative Sensitivity of Rare Earth Elements In Spark-Source Mass Spectrometry, Talanta, 17, 593, (1970).

[17] Tong, S. C., Gutenmann, W. H., St. John, L. E., Jr., and Lisk, D. J., Determination of Fluorine and Bromine in Halogenated Herbicide Residues in Soil by Spark Source Mass Spectrometry, Anal. Chem., 44, 1069 (1972).

[18] Franklin, J. C., Time-Resolved Spark-Source Mass Spectrometry; The Effect of Spark Duration on Relative Sensitivity Factors, Ion Intensity, and Precision of Analysis, Union Carbide Corporation, Nuclear Division, Y-1757, Oak Ridge, Y-12 Plant, Contract W-7405.

[19] Leipziger, F. D., Isotope Dilution Analyses by Spark Source Mass Spectrography, Anal. Chem., 37, 171 (1965).

[20] Brown, R., The Quantitative Analysis of Inorganic Pollutants in Air and Water Using Spark Source Mass Spectrometry, presented at ISIMEP, Ottawa, June 1971, AEI Scientific Apparatus, Publ. TP 36.

[21] Chupakhin, M. S., Kazakov, I. A., and Kryuchkova, O. I., Determination of Impurities in Liquids on a Spark Ion Source Mass-Spectrometer Communication 1. Analytical Technique and the Mechanism of Ion Formation, Z. Anal. Khimii, 24, 3 (1969).

[22] Brown, R. and Vossen, P. G. T., Spark Source Mass Spectrometric Survey Analysis of Air Pollution Particles, Anal. Chem., 42, 1820 (1970).

[23] Jones, R. M., Kuhn, W. F., and Varsel, C., Spark Source Mass Spectrographic Analysis of Tobacco Ash, Anal. Chem., 40, 10 (1968).

[24] Harrison, W. W., Clemena, G. G., and Magee, C. W., Forensic Applications of Spark Source Mass Spectrometry, J. of the AOAC, 54, 929 (1971).

[25] Yurachek, J. P., Clemena, G. G., and Harrison, W. W., Analysis of Human Hair by Spark Source Mass Spectrometry, Anal. Chem., 41, 1666 (1969).

[26] Harrison, W. W. and Clemena, G. G., Factors Affecting the Use of External Standards for Spark Source Mass Spectrometry, Anal. Chem., 44, 940 (1972).

[27] Cherrier, C. and Nalbantoglu, M., Determination of Trace Impurities in Mercury and Some High Purity Acids by Spark Source Mass Spectrometry, Anal. Chem., 39, 1640 (1967).

[28] Tong, S. S. C., Gutenmann, W. H., and Lisk, D. J., Determination of Mercury in Apples by Spark Source Mass Spectrometry, Anal. Chem., 41, 1872 (1969).

[29] Clegg, J. B., Millet, E. J., and Roberts, J. A., Direct Analysis of Thin Layers by Spark Source Mass Spectrography, Anal. Chem., 42, 713 (1970).

[30] Brown, R., Powers, P., and Wolstenholme, W. A., Computerized Recording and Interpretation of Spark Source Mass Spectra, Anal. Chem., 43, 1079 (1971).

[31] Socha, A. J., Analysis of Thin Films Utilizing Mass Spectrometric Techniques, Vac, Sci. Tech., 7, 310 (1970).

[32] Taylor, S. R., Geochemical Application of Spark Source Mass Spectrography-II. Photoplate Data Processing, Geochim. Cosmochim. Acta, 35, 1187 (1971).

[33] Morrison, G. H. and Rothenberg, A. M., Homogenization of Nonconducting Samples for Spark Source Mass Spectrometric Analysis, Anal. Chem., 44, 515 (1972).

[34] Taylor, S. R., Muir, P., and Kaye, M., Trace Element Chemistry of Apollo 16 Lunar Soil from Fra Mauro, Geochim. Cosmochim. Acta, 35, 975 (1971).

[35] Taylor, S. R., Geochemical Analysis by Spark Source Mass Spectrography, Geochim. Cosmochim. Acta, 29, 1243 (1965).

[36] Conzemius, R. J. and Svec, H. J., An Electrical Detection System for a Spark-Source Mass Spectrograph, Talanta, 16, 365 (1969).

[37] Morrison, G. H. and Colby, B. N., Precision of Electrical Detection Measurements of Powdered Samples in Spark Source Mass Spectrometry, Anal. Chem., 44, 1206 (1972).

[38] Kai, J. and Watanabe, M., Mass Spectrographic Determination of Impurities in Liquids, Mass Spectroscopy, 16, 241 (1968).

[39] Chastagner, P. and Tiffany, B., Analysis of Curium and Californium by Single-Exposure Spark Source Mass Spectrometry, Int. J. Mass Spectrom. Ion Phys., 9, 325 (1972).

[40] Morrison, G. H. and Kashuba, A. T., Multielement Analysis of Basaltic Rock Using Spark Source Mass Spectrometry, Anal. Chem., 41, 1842 (1969).

[41] Evans, C. A., Jr. and Morrison, G. H., Trace Element Survey Analysis of Biological Materials by Spark Source Mass Spectrometry, Anal. Chem., 40, 869 (1968).

[42] Chastagner, P., Analysis of Microsamples by Single-Exposure Spark Source Mass Spectrometry, Anal. Chem., 41, 796 (1969).

[43] Carter, J. A. and Sites, J. R., Determining PPB Mercury Concentrations Using a Spark-Source Mass Spectrometer Sample Changer, Anal. Letters, 4, 351 (1971).

[44] Taylor, J. K., Alvarez, R., Paulsen, P. J., Paulson, R. A., Rains, T. C., and Rook, H. L. Interaction of Nitrilotriacetic Acid with Suspended and Bottom Material, Water Pollution Control Research Series, 16020 GFR 07/71, U.S. Environmental Protection Agency.

[45] Taylor, C. E., McGuire, J. M., and McDaniel, W. H., Computerized Interpretation of Spark Source Mass Spectra for Water Analysis, 20th Annual Conf. on Mass Spectrometry and Allied Topics, June 4-9, 1972, Dallas, Texas.

[46] Ikeda, Y., Umayahara, A., Kubota, E., Aloyama, T., and Watanabe, E., Trace Element Analysis of Glass by High Resolution Spark Source Mass Spectrometry, 20th Annual Conf. on Mass Spectrometry and Allied Topics, June 4-9, 1972, Dallas, Texas.

[47] Morrison, G. H., Kashuba, A. T., and Rothenberg, A. M., Elemental Abundances in Lunar Materials by Spark Source Mass Spectroscopy, 18th Annual Conf. on Mass Spectrometry and Allied Topics, June 14-19, 1970, San Francisco, Calif.

[48] Socha, A. J., Updegrove, W. S., and Oro, J., Mass Spectrograph Analysis of Lunar Materials by Probe Technique, 18th Annual Conf. on Mass Spectrometry and Allied Topics, June 14-19, 1970, San Francisco, Calif.

[49] Bingham, R. A., Brown,, R., and Powers, P., On Line Analysis with a Spark Source Mass Spectrometer, 18th Annual Conf. on Mass Spectrometry and Allied Topics, June 14-19, 1970, San Francisco, Calif.

[50] Hunt, M. H., The Analysis of Non-Conducting Solids by Spark Source Mass Spectrography, 18th Annual Conf. on Mass Spectrometry and Allied Topics, June 14-19, 1970, San Francisco, Calif.

[51] Leipziger, F. D., Photographic vs. Electrical Detection for Spark Source Instruments, 18th Annual Conf. on Mass Spectrometry and Allied Topics, June 14-19, 1970, San Francisco, Calif.

[52] Socha, A. J., Baker, C. W., and Masumoto, E. M., An Electronic Detection System Utilizing Integration Techniques for a Spark Source Mass Spectrometer, 17th Annual Conf. on Mass Spectrometry and Allied Topics, May 18-23, 1969, Dallas, Texas.

[53] Sasaki, N. and Watanabe, E., The Application of Spark Source Mass Spectrometry to the Trace Element Analysis of Some Biological Materials, 13th Annual Conf. on Mass Spectrometry and Allied Topics, May 16-21, 1965, St. Louis, Missouri.

CHAPTER 4

X-RAY FLUORESCENCE AND ELECTRON MICROPROBE METHODS

Stanley D. Rasberry and Kurt F. J. Heinrich

1. X-RAY FLUORESCENCE

X-ray fluorescence analysis is noted for its applicability to a diversity of sample types and it has gained extensive industrial use for monitoring the composition of both raw materials and finished products. An introduction to the technique and descriptions of many applications are given in several books (References 1-6). The elements above atomic number 11 can be routinely determined in ores, minerals, fuels, bulk particulates, liquids, slurries, filtrates, powders, metals and other sample types. The applications of x-ray fluorescence analysis are being described in about 500 published papers per year. References 7-100 and 123-126, appended to this chapter, have been selected to represent recent applications.

The name x-ray fluorescence analysis is used to categorize several analytical techniques which have the same physical basis; inner-shell excitation of atoms induced via energy transfer from an incident flux of x-rays and the subsequent decay from excited state coupled with electron-atom recombination. The energy transfer, in both excitation and emission (decay) is dependent upon the atomic number (element) of the atom involved in the interaction. That is, an emitted fluorescent x-ray is characteristic in energy of the atom from which it is emitted. This gives the analyst a useful means of qualitatively identifying which elements are present in a specimen. As we shall see later, accurate quantitation depends in part on measuring the rate (intensity) at which x-rays of a given energy are emitted.

The apparatus necessary to x-ray fluorescence analysis includes a source of x-rays for excitation and a means of determining the rate of x-rays emitted from the specimen at discrete energies (the analyzer, detector and counting electronics). A variety of choices exists for each module of the instrument.

The excitation source may be an x-ray tube arranged to excite the specimen directly or through a filter so selected as to alter the excitation spectrum to more useful wavelengths. Another possible choice for excitation is the use of radioisotopes; here too, filters can be used. Outside the precise definition of fluorescent spectroscopy, excitation can also be effected by bombarding the specimen with electrons (10-100 keV), protons (1-200 MeV), or a variety of ions.

At the next stage in the apparatus, precise specimen positioning is required, and the excitation x-rays must be apertured so as to fall only on the specimen. The main options at this point consist of automated specimen changing or equipment for direct examination of continually flowing liquid, slurry or powder streams.

Various arrangements of collimation may be used either to aid reduction of background or improve energy resolution characteristics.

Separating the emitted x-rays into a spectrum of resolved energies is usually accomplished by one of three different means: diffraction, balanced filters, or "energy dispersive" analyzer. Diffraction of the x-ray beam by a crystal can be used to disperse the energies as an inverse function of beam-to-crystal angle. The dispersion characteristics are also a function of the lattice spacing of the crystal; but, this aspect is held constant with a given crystal selection. In the use of balanced filters, the filters are selected so that they transmit equal intensities at all energies except those between their absorption edges, and so that the energy of interest falls within this "band pass".

In both the diffractive and balanced filter modes, an x-ray detector must be employed to measure the presence and intensity of x-rays at a given energy. Scintillation detectors, gas-filled proportional detectors and gas-flow proportional detectors are used in different ranges of energies and count rates.

In the "energy dispersive" mode no physical separation of energies is used prior to the detector. Instead, energy separation is accomplished on the basis of pulse height analysis of the output signal of the detector. This is practicable because each x-ray energy produces an electronic pulse which is proportional in energy and thus susceptible to analysis. The detectors usually used in this mode are the Si(Li) solid state detectors because of their good energy resolution characteristics.

Each of the three means of energy analysis described have a large number of possible variations. This, together with the wide variety of excitation and detection possibilities, causes the number of permutations of instrument configurations to be large. One of the most generally effective arrangements for quantitative elemental analysis is shown in Figure 1. This

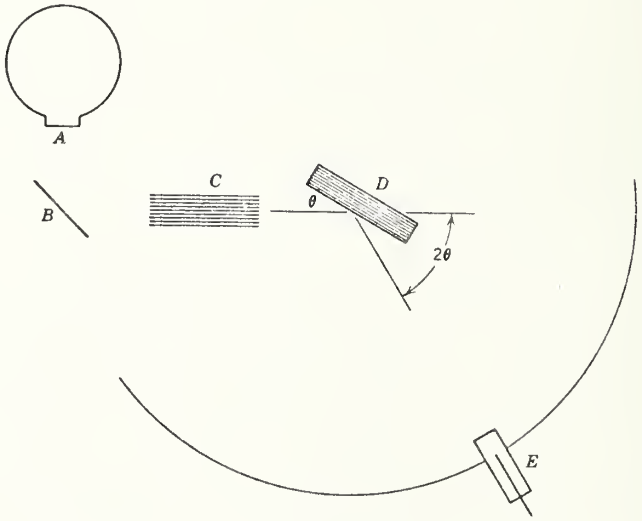

Figure 1. X-ray fluorescence analyzer. Flat crystal spectrometer geometry: (A) x-ray tube, (B) specimen, (C) collimator, (D) dispersing crystal, (E) detector, frequently preceded by a collimator. (From Reference 2)

is the arrangement which has been used in most of the applications referred to in the bibliography. We have used it at NBS in the analysis of many different types of specimens. As an example, in Figure 2 we show the x-ray spectra of two samples of liquid paint. The spectrum on the right is for a paint with presence of antimony, cadmium, strontium, arsenic and mercury six-fold greater than in the paint represented on the left. At energies (x-ray lines) characteristic of these five elements, there is a nearly proportional increase in intensity — demonstrating the feasibility of quantitative, as well as qualitative, analysis.

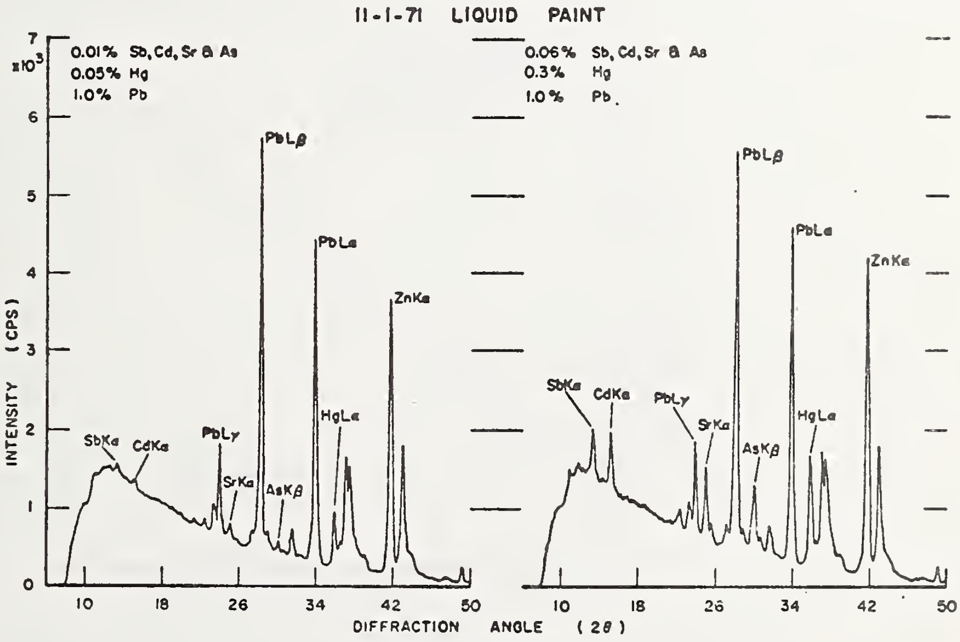

Figure 2. X-ray fluorescence spectra of liquid paints having two different levels of toxic metal content; obtained using a tungsten target tube operated at 50 kV, 50 mA, and LiF crystal and a scintillation detector.

Quantitative determination of elements which do not vary over wide ranges of concentration (more than a few percent, by weight) in specimens of nearly constant composition is accomplished by use of standard reference materials or other known "type standards". It is important for the standards to be nearly the same in composition as the unknowns because of interelement effects which will be mentioned later. An example is given in Figure 3 of a calibration curve prepared, at NBS, for the determination of lead in dry paint powder. The dry paint powder has been mixed with a common matrix to dilute the effects of differences in the remainder of the compositions.

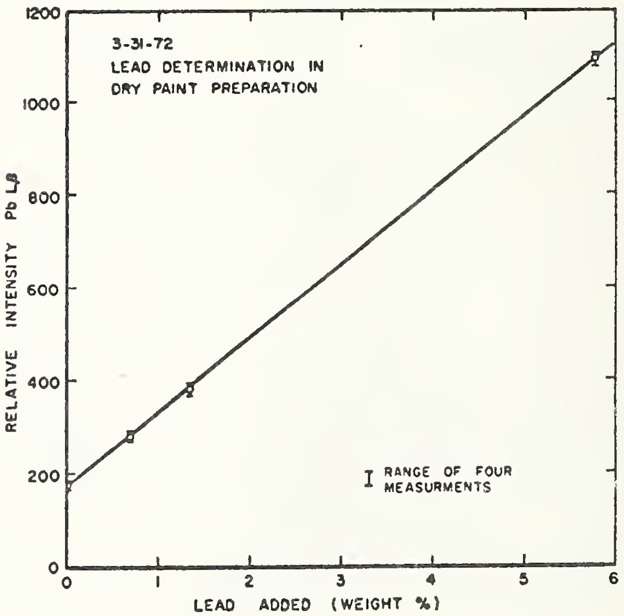

Figure 3. Calibration curve for determination of lead in dry paint powder, following preparation by dilution with a common matrix (ZnO); obtained using the same conditions as given in Figure 2.

Usually, x-ray fluorescence analysis can be performed directly on a sample with little or no preliminary treatment; this results in low labor costs. For some types of samples, notably slurries, on-stream analysis is done for control purposes using automated equipment. The detection limit for direct analysis is usually 50-1000 ppm depending on the matrix and weight of sample available. For the more sensitive elements, or by using special preconcentration techniques, lower detection limits are achievable. Normally, one or two grams of material are used when this quantity is available. However, specimens as small as a few milligrams may be analyzed, possibly with reduced sensitivity, by using special methods. In industrial examples, the precision and accuracy available have permitted the economical analysis of such materials as steel, aluminum, glass and portland cement powder on an essentially real-time basis. The accuracy required in industry is typically ±1/2 percent to ±1 percent for the major elements, ±2 percent for the minor elements, and ±10 percent for the trace constituents.

X-ray fluorescence equipment is available for simultaneous determination of as many as ten or more elements, in the same sample, in a two-minute measurement period. Virtually every phase of the technique is susceptible to automation, from specimen preparation and insertion into the instrument through all measurement aspects, data collection, computation, interpretation and display. Especially when large volumes of analyses are done, automation is economically attractive owing to substantially decreasing labor costs. The instrument operators may be high school, vocational school or junior college-trained technicians; however, the supervision of the effort should be in the hands of a graduate chemist, chemical engineer or equivalent.

Interferences of two different types can occur in x-ray fluorescence. In the first (line interferences), an x-ray line of the analyte may be so near a line produced by another element that the two are not resolved by the spectrometer. Usually, this problem can be solved by selecting another x-ray line of the analyte to measure. The second kind of interference (matrix interelement effects) is caused when large differences in composition exist among the various standards and unknowns. The intensity of the x-ray line of the analyte is influenced not only by the analyte concentration, but also by the composition of the matrix (other elements). Correction procedures, either through chemical preparation or mathematical data manipulation are available to resolve this type of interference. Standard Reference Materials play a key role in the accurate calibration of x-ray fluorescence analysis.

A. Application to Matrices of Environmental Interest

1. Fly Ash and Incinerator Particulates. (References 7-19) Methods for the x-ray fluorescence analysis of fly ash and incinerator particulates were not actively researched until about five years ago. Since that time, extensive work has

been done on the subject. As can be seen in the appended summary sheet, x-ray fluorescence methods are applicable for the determination of 24 of the 28 elements of principal interest. In routine direct analysis, the cost of determining one element should not exceed $1.00. Lower concentrations can be obtained by chemical pretreatment of the sample, with an attendant increase in cost (see References 18 and 19). The need for standard reference materials seems to be especially pressing for fly ash and incinerator particulate matrices.

2. Coal. (References 20-23) L. T. Kiss (21) has made one of the best and most thorough studies of x-ray fluorescence analysis of coal presently available. Using a procedure of drying, fine-grinding and briquetting ten-gram samples of coal, x-ray measurement, and a special interelement correction procedure, Kiss was able to accurately determine from 0.02 percent to 3.90 percent of iron, titanium, calcium, potassium, chlorine, sulfur, silicon and aluminum in coal. Both synthetically prepared and chemically analyzed standards are used in calibration.

3. Oil. (References 24-37) X-ray fluorescence analysis of oils and gasolines is one of the oldest routine applications of the method — dating back to the 1940's. Outstanding work has been done in this area by Birks, Brooks, Friedman and Roe (34), Dwiggins and Dunning (27-28), Hale and King (26) and Gunn (24-25). All elements above sodium can be determined

in oil by x-ray fluorescence methods. Particular attention has been given to lead, bromine, molybdenum, nickel, iron, manganese, titanium, vanadium, zinc, calcium, and barium. Hale and King (26) report direct determination of nickel at the 0.1 ppm level, and Bergmann, Ehrhardt, Granatelli and Janik (30) report sub-ppm determinations using ion exchange preconcentration. The method is finding increased use (including work at NBS) in monitoring wear metals in engine and gearcase oils.

4. Ores, Minerals and Cement. (References 38-54) X-ray fluorescence analysis has found wide industrial acceptance in these areas over the past twenty years. This is especially true in the cement industry, where tens of thousands of determinations are performed each day using x-ray fluorescence spectrometers, many of which are highly automated. The work of Rose and Brown (38), Rose, Adler and Flanagan (44) and Campbell and Thatcher is especially important to the mining industry. Bean (48-49) and Andermann (50) are widely cited among investigators of x-ray fluorescence methods for the analysis of cement. When matrix variations are large, physically corrective techniques, such as dilution or mathematical treatment to correct the results are usually required. The need for standards is especially large in this area, and many have been produced by NBS, the most recent being seven new SRM's for portland cement to replace and supplement five others which were issued ten years ago.

5. Metals and Alloys. (References 55-79) Similar to the case of ores, minerals and cement, this area has been widely developed and used in industry over the past twenty years — with significant improvement and further extension of application over the last five to ten years. The of literature dealing with the analysis of metals and alloys by x-ray fluorescence is large (approximately 10,000 papers). The references given here are representative, but hardly do more than scratch the surface. The usual range for direct, accurate analysis is 0.01 percent to 95.0 percent for the elements above sodium in atomic weight. Research and development is active in this area, especially concentrating in: lower detection limits, more complete automation, more accurate standardization, and improved mathematical treatment. Several hundred Standard Reference Materials for metals and alloys have been issued by NBS. Alloy reference standards are also sold by U.S. Steel, Carpenter Technology, Brammer Standards, Alcoa and others.

6. Organometallics. (References 80-82, also see papers in section: Oil) The analysis of metallo-organic compounds is not a common subject in the x-ray fluorescence literature. However, metallo-organic compounds are used as additives in the preparation of synthetic oil standards. The literature pertinent to the x-ray fluorescence analysis of oil is described in the appropriate section. NBS has issued 24

metallo-organic compounds primarily to be used for the calibration of spectrochemical equipment used in the determination of wear metals in lubricating oil.

7. Slurry Streams, and Feeds and Sediments in Flotation Processes. (References 83-94) Smallbone (85 and 87) and Smallbone and Davidson (84 and 86) have been leaders in the design and construction of the special sample handling apparatus needed for "on-line" x-ray fluorescence applications. Calibration for these techniques is made difficult by the variability of water content in the moving material; corrections are required. Sampling is also an important aspect of the problem. Standardization is difficult, because to simulate the material under analysis requires flowing a large volume of standard through the on-line sample handling apparatus. These problems cause undesirable losses in accuracy; further R and D appears to be needed in this area.

8. Slags and Glass. (References 95-100) An increasing amount of quality control analysis in the glass industry is done by x-ray fluorescence analysis. It is also a popular method for evaluating slags. Glasses are analyzed directly on solid material, with calibration by standards. NBS is supplying two Standard Reference Materials of solid glass and the ASTM is assisting in establishing several more on an inter-company basis. Until now, most companies have had only standards made in their own plants. The x-ray method is in a good state of development relative to glass analysis.

Slags are usually treated with preparation techniques similar to those used for ores: crushing and briquetting, diluting and briquetting or diluting and fusion. The preparation of standards must follow the same process.

2. ELECTRON PROBE MICROANALYSIS

Electron probe microanalysis has been available, with commercially produced instruments, for about 15 years. During that time many industrial applications have been described in the literature. A survey of these is given in Refs. 101-122.

Electron probe microanalysis is the sum of procedures using a focused electron beam (of energy between 1 and 50 keV) to obtain, from the zone of beam impact upon a specimen, information concerning its properties. This is achieved in an instrument similar in some aspects to the electron microscope. Electrons emitted from a heated tungsten wire are focused into a beam of a diameter of less than 0.5 μm. This beam is directed toward the specimen. The interaction of the specimen with the impinging electron beam results in the emission of x-ray lines from the microscopic region of the specimen which has been excited by the electrons. The characteristic x-ray spectra emitted by the specimen reveal its elemental composition.

The emitted x-ray lines can be observed, and their intensities measured, by means of single-bent crystal spectrometers. The instrument at NBS has three such spectrometers, so that three elements can be measured simultaneously. The wavelength range is from 1 to 100 Å; this permits the observation and analysis of all elements of atomic number above 5, and with high sensitivity for the elements of atomic number above 10. Another device installed in the NBS electron probe is the energy dispersive solid state detector. This device permits the simultaneous detection of all elements of atomic number above 11, and thus provides for a rapid means for qualitative and semiquantitative analysis, which is particularly useful in the analysis of small particles.

Other phenomena (emission of backscattered and secondary electrons, cathodoluminescence, etc.) also produce useful information. The analyzed region on the specimen which is excited by the electron beam is usually about 2 x 2 x 2 μm. Since Cosslett and Duncumb (128) introduced the scanning beam technique in electron probe microanalysis, the instrument has become a microscope as well as a spectrometer. The interactions between scanning electron microscopy and x-ray spectrometry account for the great versatility of this instrument. It has found wide industrial application both for the analysis of free-standing micro-particulates and for microscopic features on the surfaces of bulk materials.

The forte of the electron probe is microanalysis (small size) as opposed to trace analysis (low concentration); however, detection limits between 100 and 1000 ppm are available for most elements. Accuracies of ±5 percent, or better, are routinely available and careful, quantitative work can produce accuracies of ±2 percent. The precision of measurement, for elements above 1 percent in concentration, is generally ±1 percent or better.

Sample preparation depends on the nature of the specimen. If the specimen is larger than one inch in diameter, a sample must be cut so that it will be small enough (one-inch diameter) to load in the instrument. Discrete micro-particulates can be isolated, mounted and restrained. Quantitative analysis of metals requires a flat polish, equivalent to that obtained with 1/4-μm diamond polishing compound. Non-conductive specimens are given a sub-μm coating of a conductor (usually carbon) in a vacuum evaporator so that static charging will not occur when the samples are subjected to the electron beam. In some cases, especially for qualitative work, no sample preparation is required.

The cost for purchase of an electron probe microanalyzer, auxiliary equipment and sample preparation facilities is about $150K to $200K. Operational cost for an electron probe laboratory, including labor costs, may be expected to range between $250 and $500 per day. A single element determination on a single point on a sample requires about one-half hour; economies may result when several elements are determined at several points on the same sample. As with x-ray fluorescence, the instrument operators may be non-degreed technicians, but supervision should be in the hands of a graduate chemist, or equivalent.

The conditions for electron probe microanalysis and the results to be expected are quite similar for all sample types which can be analyzed, therefore, a single guideline for application is appended. Usually the electron probe analysis is considered applicable to particulates isolated from fly ash or from incinerators; or even, particulates from slurry streams or in sediments from flotation processes. In addition, it is applicable to analyses in coal, ores, minerals, cement, metals, alloys, slags and glasses. To the best of our knowledge, it has not been applied to analysis of oil or organometallics. It would be feasible, however, to perform such analyses on solid particulate wear residues in lubricating oils.

Table 1. Analysis of Fly Ash and Incinerator Particulates by X-Ray Fluorescence

Element[a]	Expected Conc'n. (ppm)	Accuracy (%)	Time to Prepare Sample (min)	Sample Size (g)	Detection[b] Limit (ppm)	Cost[c] Per Analysis ($)	References
Hg	(d)	5-25	5	1-10	500	1-5	See 7-19, especially:
Cd	10-100	15	"	"	100	"	
As	100	15	"	"	100	"	
V	500	5	"	"	50	"	
Mn	1000	5	"	"	50	"	
Ni	500	5	"	"	10	"	
Sb	10	25	"	"	100	"	
Cr	100	15	"	"	50	"	
Zn	5000	5	"	"	50	"	14
Cu	1000	5	"	"	50	"	
Pb	5000	5	"	"	200	"	12,16,17
Se	(d)		"	"	100	"	
Ag	(d)		"	"	100	"	
Sn	100	15	"	"	100	"	
Fe	1-10%	5	"	"	50	"	
Sr					200		
Na	(e)	15	"	"	1-2%	"	
K	(e)	5	"	"	200	"	
Ca	(e)	5	"	"	100	"	
Si	(e)	5	"	"	200	"	
Mg	(e)	5	"	"	1000	"	
U	(d)		"	"	500	"	
Th	(d)		"	"	500	"	
S	(e)	5	"	"	200	"	7,19

(a) Determination of Be, B, F, Li not feasible by XRF.
(b) See text for equipment required, manpower skills, and interferences expected.
(c) Ten elements may be determined for $10-50 total, in routine analysis.
(d) Expected levels not known. May be 1-10 ppm or less.
(e) Major constituents.

Table 2. Analysis of Coal by X-Ray Fluorescence

Element[a]	Expected Conc'n. (ppm)	Accuracy (%)	Time to Prepare Sample (min)	Sample Size (g)	Detection[b] Limit (ppm)	Cost[c] Per Analysis ($)	References
Hg			30	10	500	5-10	See 20-23, especially:
Cd			"	"	100		
As			"	"	100		
V			"	"	50		
Mn			"	"	50		
Ni			"	"	10		
Sb			"	"	100		
Cr			"	"	50		
Zn			"	"	50		
Cu			"	"	50		
Pb			"	"	200		
Se			"	"	100		
Ag			"	"	100		
Sn			"	"	100		
Fe	0.5-10%	5	"	"	50		21,23
Sr			"	"	200		
Na	0.01-3%	25	"	"	1-2%		23
K	0.01-0.5%	25	"	"	200		21,23
Ca	0.1-10%	5	"	"	100		21,23
Si	0.5-10%	5	"	"	200		21,23
Mg	0.1-1%	5	"	"	1000		23
U					500		
Th					500		
S	0.3-6%	5	"	"	200		20,23
Al	0.5-10%	5	"	"	200		21,23
Ti	2000	5	"	"	10		21,23
Cl	0.04-0.20	15	"	"	200		21

(a) Determination of Be, B, F, Li not feasible by XRF.
(b) See text for equipment required, manpower skills, and interferences expected.
(c) Ten elements may be determined for $50-100 total, in routine analysis.

Table 3. Analysis of Oil and Organometallics by X-Ray Fluorescence

Element(a)	Expected Conc'n. (ppm)	Accuracy (%)	Time to Prepare Sample (min)	Sample Size (g)	Detection(b) Limit (ppm)	Cost(c) Per Analysis ($)	References
Hg			5	10	500	4-10	See 24-37,80-82, especially:
Cd			"	"	100	"	
As			"	"	100	"	
V	100-500	5	"	"	2	"	28
Mn	5%	1	"	"	50	"	35
Ni	0.1-100	5	"	"	0.1	"	24,27
Sb			"	"	100	"	
Cr			"	"	50	"	
Zn	100-500	15	"	"	50	"	31
Cu			"	"	50	"	
Pb	500	15	"	"	200	"	31
Se			"	"	100	"	
Ag			"	"	100	"	
Sn			"	"	100	"	
Fe	1-100	15	"	"	1	"	28
Sr			"	"	200	"	
Na			"	"	1-2%	"	
K			"	"	200	"	
Ca	0.1-1%	5	"	"	100	"	31
Si			"	"	200	"	
Mg			"	"	1000	"	
U			"	"	500	"	
Th			"	"	500	"	
S	0.1-5%	15	"	"	100	"	28
Al			"	"	200	"	
Ti			"	"	10	"	

(a) Determination of Be, B, F, Li not feasible by XRF.
(b) See text for equipment required, manpower skills, and interferences expected.
(c) Five elements may be determined for $20-50 total, in routine analysis.

Table 4. Analysis of Ores, Minerals and Cements by X-Ray Fluorescence

Element[a]	Expected[b] Conc'n. (ppm)	Accuracy[c] (%)	Time to Prepare Sample (min)	Sample Size (g)	Detection[d] Limit (ppm)	Cost[e] Per Analysis ($)	References
Hg		5	5-30	2-10	500	1-10	See 38-54, especially
Cd		"	"	"	100	"	
As		"	"	"	100	"	
V		"	"	"	50	"	
Mn		"	"	"	50	"	
Ni		"	"	"	10	"	
Sb		"	"	"	100	"	
Cr		"	"	"	50	"	
Zn		"	"	"	50	"	
Cu		"	"	"	50	"	
Pb		"	"	"	200	"	
Se		"	"	"	100	"	
Ag		"	"	"	100	"	
Sn		"	"	"	100	"	
Fe		"	"	"	50	"	
Sr		"	"	"	200	"	
Na		"	"	"	1-2%	"	
K		"	"	"	200	"	
Ca		"	"	"	100	"	
Si		"	"	"	200	"	
Mg		"	"	"	1000	"	
U		"	"	"	500	"	
Th		"	"	"	500	"	
S		"	"	"	200	"	

(a) Determination of Be, B, F, Li not feasible with XRF.
(b) Concentrations depend on samples and stages of processing.
(c) Accuracy generally ±5 percent for main elements.
(d) See text for equipment required, manpower skills, and interferences expected.
(e) Cost in direct, automated systems less than $1 per element; in manual systems with preparation, $10 per element.

Table 5. Analysis of Metals and Alloys by X-Ray Fluorescence

Element[(a)]	Expected[(b)] Conc'n. (ppm)	Accuracy[(c)] (%)	Time to Prepare Sample (min)	Sample Size	Detection[(d)] Limit (ppm)	Cost[(e)] Per Analysis ($)	References
Hg		2-5	1-10	Usually Bulk	500	1	See 55-79
Cd		"	"		100	"	
As		"	"		100	"	
V		"	"		50	"	
Mn		"	"		50	"	
Ni		"	"		10	"	
Sb		"	"		100	"	
Cr		"	"		50	"	
Zn		"	"		50	"	
Cu		"	"		50	"	
Pb		"	"		200	"	
Se		"	"		100	"	
Ag		"	"		100	"	
Sn		"	"		100	"	
Fe		"	"		50	"	
Sr		"	"		200	"	
Na		"	"		1-2%	"	
K		"	"		200	"	
Ca		"	"		100	"	
Si		"	"		200	"	
Mg		"	"		1000	"	
U		"	"		500	"	
Th		"	"		500	"	
S		"	"		200	"	

(a) Determination of Be, B, F, and Li not feasible with XRF.
(b) Concentrations depend on metal samples.
(c) Accuracy generally ±2-5 percent for main and minor elements.
(d) See text for equipment required, manpower skills, and interferences expected.
(e) In industrial applications, usually less than $1 per element.

Table 6. Analysis of Slurry Streams, Feeds and Sediments by X-Ray Fluorescence

Element[(a)]	Expected[(b)] Conc'n. (ppm)	Accuracy[(c)] (%)	Time to Prepare Sample (min)	Sample Size (g)	Detection[(d)] Limit (ppm)	Cost[(e)] Per Analysis ($)	References
Hg		15	0-30	1-10	500	1	See 83-94
Cd		"	"	"	100	"	
As		"	"	"	100	"	
V		"	"	"	50	"	
Mn		"	"	"	50	"	
Ni		"	"	"	10	"	
Sb		"	"	"	100	"	
Cr		"	"	"	50	"	
Zn		"	"	"	50	"	
Cu		"	"	"	50	"	
Pb		"	"	"	200	"	
Se		"	"	"	100	"	
Ag		"	"	"	100	"	
Sn		"	"	"	100	"	
Fe		"	"	"	50	"	
Sr		"	"	"	200	"	
Na		"	"	"	1-2%	"	
K		"	"	"	200	"	
Ca		"	"	"	100	"	
Si		"	"	"	200	"	
Mg		"	"	"	1000	"	
U		"	"	"	500	"	
Th		"	"	"	500	"	
S		"	"	"	200	"	

(a) Determination of Be, B, F, Li not feasible with XRF.
(b) Concentrations depend on materials being analyzed.
(c) Accuracies frequently not better than ±15 percent because of calibration difficulties.
(d) See text for equipment required, manpower skills, and interferences expected.
(e) In industrial applications, usually less than $1 per element.

Table 7. Analysis of Slags and Glasses by X-Ray Fluorescence

Element(a)	Expected(b) Conc'n. (ppm)	Accuracy(b) (%)	Time to Prepare Sample (min)	Sample Size (g)	Detection(c) Limit (ppm)	Cost(d) Per Analysis ($)	References
Hg			5-30	2-10	500	1-10	See 95-100
Cd	(e)		"	"	100	"	
As			"	"	100	"	
V	(e)		"	"	50	"	
Mn	(e)		"	"	50	"	
Ni	(e)		"	"	10	"	
Sb	(e)		"	"	100	"	
Cr	(e)		"	"	50	"	
Zn	(e)		"	"	50	"	
Cu	(e)		"	"	50	"	
Pb	0-5%	5	"	"	200	"	
Se	(e)		"	"	100	"	
Ag			"	"	100	"	
Sn	(e)		"	"	100	"	
Fe	0-3%(f)	5	"	"	50	"	
Sr	(e)		"	"	200	"	
Na	0-20%	15	"	"	1-2%	"	
K	0-5%	15	"	"	200	"	
Ca	(g)	5	"	"	100	"	
Si	(g)	1	"	"	200	"	
Mg	0.01-5%	5	"	"	1000	"	
U			"	"	500	"	
Th			"	"	500	"	
S			"	"	200	"	

(a) Determination of Be, B, F, Li not feasible with XRF.

(b) Elemental concn. and accuracy of determination are sample-dependent.

(c) See text for equipment required, manpower skills, and interferences expected.

(d) Direct, automated systems less than $1 per element; manual systems with preparation, $10 per element.

(e) Possibly present in both slags and glasses.

(f) Higher in slags.

(g) Major constituent in slags and glasses.

Table 8. Analysis of Particulates by the Electron Probe Microanalyzer

Element	Expected(a) Conc'n. (ppm)	Accuracy(a) (%)	Detection(b) Limit (ppm)	Cost(c) Per Analysis ($)	References
Hg			0.1%	5-50	See 101-122
Be				"	
Cd			200	"	
As			200	"	
V			100	"	
Mn			100	"	
Ni			100	"	
Sb			200	"	
Cr			100	"	
Zn			100	"	
Cu			100	"	
Pb			200	"	
Se			200	"	
B				"	
F				"	
Li				"	
Ag			200	"	
Sn			200	"	
Fe			100	"	
Sr			200	"	
Na			1%	"	
K			200	"	
Ca			100	"	
Si			100	"	
Mg			500	"	
U			500	"	
Th			500	"	

(a) Elemental concentration and accuracy of determination are sample-dependent.
(b) See text for equipment required, time to prepare sample, sample size, manpower skills, and interferences.
(c) Automated systems about $5 per element, manual systems with preparation about $50 per element.

References

Books Related to X-ray Fluorescence Analysis

1. H. A. Liebhafsky, H. G. Pfeiffer, E. H. Winslow and P. D. Zemany, "X-ray Absorption and Emission in Analytical Chemistry," Wiley, New York (1960).

2. L. S. Birks, "X-ray Spectrochemical Analysis," 2nd Ed., Interscience, New York (1969).

3. R. Jenkins and J. L. De Vries, "Practical X-ray Spectrometry," Springer-Verlag, New York (1969).

4. E. P. Bertin, "Principles and Practice of X-ray Spectrochemical Analysis," Plenum, New York (1970).

5. R. O. Müller, trans. by K. Keil, "Spectrochemical Analysis by X-ray Fluorescence," Plenum, New York (1972).

6. K. F. J. Heinrich, C. S. Barrett, J. B. Newkirk and C. O. Ruud, eds., "Advances in X-ray Analysis," Vol. 5, Plenum, New York (1972). The preceding 14 volumes of this series also contain numerous articles on the use of x-ray fluorescence analysis.

Fly Ash and Incinerator Particulates

7. S. C. Goadby and J. F. Stephens, "Determination of Sulphur in Fly-ash by X-ray Emission Spectroscopy," Fuel 46, 19 (1967).

8. J. Leroux and M. Mahmud, "Flexibility of X-ray Emission Spectrography as Adapted to Microanalysis of Air Pollutants," J. Air. Poll. Control Assoc. 20, 402 (1970).

9. C. H. Anderson, "Application of the VXQ-72000 X-ray Spectrometer to the Analysis of Air Particulates," Applied Research Laboratories Methods Report 825.91, Sunland, Calif. (1971).

10. F. S. Goulding and J. M. Jaklevic, "Trace Element Analysis by X-ray Fluorescence," Lawrence Berkeley Laboratory, Report UCRL-20625 (May 1971).

11. D. A. Landis, F. S. Goulding and B. V. Jarrett, "Some Aspects of X-ray Fluorescence Spectrometers for Trace Element Analysis," Lawrence Berkeley Laboratory, Report LBL-320 (Sept. 1971).

12. J. M. Jaklevic and F. S. Goulding, "Semiconductor Detector X-ray Fluorescence Spectrometry Applied to Environmental and Biological Analysis," Lawrence Berkeley Laboratory, Report LBL-743 (Mar. 1972).

13. R. D. Giauque, F. S. Goulding, J. M. Jaklevic and R. H. Pehl, "Trace Element Analysis with Semiconductor Detector X-ray Spectrometers," Lawrence Berkeley Laboratory, Report LBL-647 (July 1972).

14. J. C. Wagner, E. H. Bicknese and F. R. Bryan, "X-ray Determination of Zinc in Basic-Oxygen Flue Dust and Blast-Furnace Sinter," Appl. Spectrosc. 21, 176 (1967).

15. T. R. Dittrich and C. R. Cothern, "Analysis of Trace Metal Particulates in Atmospheric Samples Using X-ray Fluorescence," J. Air. Poll. Control Assoc. 21, 716 (1971).

16. H. R. Bowman, J. G. Conway and F. Asaro, "Atmospheric Lead and Bromine Concentration in Berkeley, Calif. (1963-1970)," Envir. Sci. and Tech. 6, 558 (1972).

17. P. Greenfelt, Å. Åkerström and C. Brosset, "Determination of Filter-Collected Airborne Matter by X-ray Fluorescence," Atmos. Envir. 5, 1 (1971).

18. C. L. Luke, "Determination of Traces of Lithium, Beryllium or Phosphorus by X-ray Analysis," Anal. Chim. Acta 45, 365 (1969).

19. C. L. Luke, "Determination of Traces of Fluorine or Sulfur by X-ray Analysis," Anal. Chim. Acta 43, 245 (1968).

Coal

20. M. Berman and S. Ergun, "Analysis of Sulphur in Coals by X-ray Fluorescence," Fuel 47, 285 (1968).

21. L. T. Kiss, "X-ray Fluorescence Determination of Brown Coal Inorganics," Anal. Chem. 38, 1731 (1966).

22. E. Davidson, A. W. Gilkerson and S. G. Shequen, "X-ray Fluorescence Analysis with a New High Speed Multichannel Instrument," Reprint from Applied Research Laboratories, Sunland, Calif. (1965).

23. C. H. Anderson and R. E. Jones, "Determination of Inorganic Constituents of Coal by X-ray Fluorescence," Reprint from Applied Research Laboratories, Sunland, Calif. (1968).

Oil

24. E. L. Gunn, "Problems of Direct Determination of Trace Nickel in Oil by X-ray Emission Spectrography," Anal. Chem. 36, 2086 (1964).

25. E. L. Gunn, "Absorption Effects in X-ray Fluorescence Measurement of Elements in Oil," Advan. in X-ray Anal. 6, 403 (1963).

26. C. C. Hale and W. H. King, Jr., "Direct Nickel Determinations in Petroleum Oils by X-ray at the 0.1-P.P.M. Level," Anal. Chem. 33, 74 (1961).

27. C. W. Dwiggins, Jr. and H. N. Dunning, "Quantitative Determination of Nickel in Oils by X-ray Spectrography," Anal. Chem. 31, 1040 (1959).

28. C. W. Dwiggins, Jr. and H. N. Dunning, "Quantitative Determination of Traces of Vanadium, Iron, and Nickel in Oils by X-ray Spectrography," Anal. Chem. 32, 1137 (1960).

29. C. C. Kang, E. W. Keel and E. Solomon, "Determination of Traces of Vanadium, Iron, and Nickel in Petroleum Oils by X-ray Emission Spectrography," Anal. Chem. 32, 221 (1960).

30. J. G. Bergmann, C. H. Ehrhardt, L. Granatelli and J. L. Janik, "Determination of Sub-PPM Nickel and Vanadium in Petroleum by Ion Exchange Concentration and X-ray Fluorescence," Anal. Chem. 39, 1258 (1967).

31. W. E. Burke, L. S. Hinds, G. E. Deodato, E. D. Sager, Jr. and R. E. Borup, "Internal Standard X-ray Spectrographic Procedure for the Determination of Calcium, Barium, Zinc and Lead in Hydrocarbons," Anal. Chem. 36, 2404 (1964).

32. E. N. Davis and R. A. Van Nordstrand, "Determination of Barium, Calcium and Zinc in Lubricating Oils - Use of Fluorescent X-ray Spectroscopy," Anal. Chem. 26, 973 (1954).

33. E. N. Davis and B. C. Hoeck, "X-ray Spectrographic Method for the Determination of Vanadium and Nickel in Residual Fuels and Charging Stocks," Anal. Chem. 27, 1880 (1955).

34. L. S. Birks, E. J. Brooks, H. Friedman and R. M. Roe, "X-ray Fluorescence Analysis of Ethyl Fluid in Aviation Gasoline," Anal. Chem. 22, 1258 (1950).

35. J. L. Caley, "The Use of X-ray Emission Spectrography for Petroleum Product Quality and Process Control," Advan. in X-ray Analysis 6, 396 (1963).

36. R. Jenkins, "Applications of X-ray Fluorescence Analysis in the Oil Industry," J. Inst. Petroleum 48, 246 (1962).

37. D. Jovanović, "Development of an X-ray Emission Spectrography Method for the Determination of Molybdenum in Oils," Anal. Chem. 42, 775 (1970).

Ores, Minerals and Cement

38. H. J. Rose and R. Brown, "X-ray Fluorescence Analysis of Niobate-Tantalate Ore Concentrates," Advan. in X-ray Analysis 7, 598 (1964).

39. A. P. Langheinrich, J. W. Forster and T. A. Linn, Jr., "Energy Dispersion X-ray (EDX) Analysis in the Non-Ferrous Mining Industry," Analysis Inst. 9, F-3 (1971).

40. R. S. Rubinovich, "Determination of Iron in Rocks and Ores by X-ray Fluorescence," Inderst. Lab. 30, 539 (1964).

41. Anon. "The Application of the ARL Model 72000 X-ray Quantometer to the Analysis of Agglomerates, Slags and Ores," Reprint from Applied Research Laboratories, Sunland, Calif. (1972).

42. B. P. Fabbi and W. J. Moore, "Rapid X-ray Fluorescence Determination of Sulfur in Mineralized Rocks from the Bingham Mining District, Utah," Appl. Spectrosc. 24. 427 (1970).

43. B. P. Fabbi, "X-ray Fluorescence Determination of Barium and Strontium in Geologic Samples," Appl. Spectrosc. 25, 316 (1971).

44. H. J. Rose, Jr., I. Adler and F. J. Flanagan, "Suggested Method for Spectrochemical Analysis of Rocks and Minerals Using an X-ray Spectrometer, E-2 SM 11-13," in Methods for Emission Spectrochemical Analysis, 5th Ed., p. 778, ASTM, Philadelphia (1968).

45. G. K. Czamanske, J. H. Hower and R. C. Millard, "Non-proportional, Non-linear Results from X-ray Emission Techniques Involving Moderate-Dilution Rock Fusion," Geochim. et Cosmochim. Acta 30, 745 (1966).

46. K. Norrish and J. T. Hutton, "An Accurate X-ray Spectrograph Method for the Analysis of a Wide Range of Geological Samples," Geochim. et Cosmochim. Acta 33, 431 (1969).

47. I. C. Stone, Jr. and K. A. Rayburn, "X-ray Spectrographic Determination of Rare Earths in Silica-Alumina Catalysts," Anal. Chem. 39, 357 (1967).

48. B. L. Bean, "A Method of Producing Sturdy Specimens of Pressed Powders for Use in X-ray Spectrochemical Analysis," Appl. Spectrosc. 20, 191 (1966).

49. B. L. Bean and B. W. Mulligan, "X-ray Spectrochemical Analysis of Materials: Cement and Dental Alloys," ASTM-STP 373, 25 (1965).

50. G. Andermann, "Suggested Method for Spectrochemical Analysis of Cement Raw Mix by the Lithium Tetraborate Fusion Technique Using an X-ray Spectrometer," in Methods for Emission Spectrochemical Analysis, 5th Ed., p. 706, ASTM, Philadelphia (1968).

51. H. T. Dryer and H. Renton, "Influence of the Origin of Raw Materials on the X-ray Analysis of Cements," Developments in Applied Spectrosc. 4, 83 (1964).

52. W. J. Campbell and J. W. Thatcher, "Determination of Calcium in Wolframite Concentrates by Fluorescence X-ray Spectrography," U.S. Bur. of Mines Rept. of Investigation 5416 (1958).

53. D. F. Sermin, "The Application of the ARL 72000 X-ray Quantometer to the Analysis of Raw Cement Materials," Reprint from Applied Research Laboratories, Sunland, Calif. (1969).

54. D. F. Sermin, "The Application of the ARL X-ray Quantometer to the Analysis of Fused Cement Clinker," Reprint from Applied Research Laboratories, Sunland, Calif. (1969).

Metals and Alloys

55. E. F. Spano, T. E. Green and W. J. Campbell, "Evaluation of a Combined Ion Exchange X-ray Spectrographic Method for Determining Trace Metals in Tungsten," U.S. Bur. of Mines Report of Investigation 6565 (1964).

56. C. A. Kienberger and A. R. Flynn, "Determination of Metallic Impurities in Aluminum by X-ray Fluorescence," U.S. AEC Research and Development Report K-1638 (1966).

57. W. W. Houk and L. Silverman, "Determination of Iron, Chromium and Nickel by Fluorescent X-ray Analysis," Anal. Chem. 31, 1069 (1959).

58. C. M. Davis and G. R. Clark, "X-ray Spectrographic Analysis of Nickel-Containing Alloys with Varied Sample Forms," Appl. Spectrosc. 4, 123 (1958).

59. R. M. Brissey, "Analysis of High Temperature Alloys by X-ray Fluorescence," Anal. Chem. 25, 190 (1953).

60. J. D. Eick, H. J. Caul, D. L. Smith and S. D. Rasberry, "Analysis of Gold and Platinum Group Alloys by X-ray Emission with Correction for Interelement Effects," Appl. Spectrosc. 21, 324 (1967).

61. S. D. Rasberry, H. J. Caul and A. Yezer, "X-ray Fluorescence Analysis of Silver Dental Alloys with Correction for a Line Interference," Spectrochim. Acta 23B, 345 (1968).

62. A. Chow and F. E. Beamish, "Determination of Gold by X-ray Fluorescence Methods," Talanta 13, 539 (1966).

63. K. Hirokawa, "Determination of Impurities in Some Non-Ferrous Metals by Fluorescent X-ray Spectroscopy," Science Repts. of the Res. Inst. Tohaku Univ. A-13, 263 (1961). English.

64. W. M. MacNevin and E. A. Hakkila, "Fluorescent X-ray Spectroscopic Estimations of Palladium, Platinum, Rhodium and Iridium," Anal. Chem. 29, 1019 (1957).

65. L. S. Birks and E. J. Brooks, "Hafnium-Zirconium and Tantalum-Columbium Systems," Anal. Chem. 22, 1017 (1950).

66. W. J. Campbell and H. E. Marr III, "Identification and Analyses of Copper-Base Alloys by Fluorescent X-ray Spectrography," U.S. Bur. of Mines Rept. of Investigation 7635 (1972).

67. A. Carnevale and A. J. Lincoln, "An X-ray Fluorescent Method for the Determination of Copper in Silver-Copper Alloys," Dev. in Appl. Spectrosc. 5, 113 (1966).

68. T. J. Cullen, "Briquetted Copper Alloy Drillings as a Sample for X-ray Spectroscopy," Anal. Chem. 33, 1343 (1961).

69. R. Alvarez and R. Flitsch, "Accuracy of Solution X-ray Spectrometric Analysis of Copper-Base Alloys," NBS Misc. Publ. 260-5 (1965).

70. R. E. Michaelis, R. Alvarez and B. A. Kilday, "Determination of Minor Constituents in Low-Alloy Steels by X-ray Fluorescence Analysis," J. of Res. Nat. Bur. of Standards 65C, 71 (1961).

71. B. A. Kilday and R. E. Michaelis, "Determination of Lead in Leaded Steels by X-ray Spectroscopy," Appl. Spectrosc. 16, 136 (1962).

72. R. W. Taylor, "X-ray Spectrochemical Determination of Niobium and Tantalum in High-Alloy and Stainless Steel," Dev. in Appl. Spectrosc. 4, 65 (1964).

73. G. E. Hicho, H. Yakowitz, S. D. Rasberry and R. E. Michaelis, "A Standard Reference Material Containing Nominally Four Percent Austenite," Adv. in X-ray Anal. 14, 78 (1971).

74. S. D. Rasberry, "Application of Computers in Electron Probe and X-ray Fluorescence Analysis," Adv. in X-ray Anal. 15, 56 (1972).

75. L. Bäckerud, "Determination of Copper in Complex Brasses by X-ray Fluorescence Spectroscopy," Appl. Spectrosc. 21, 315 (1967).

76. D. F. Sermin, "The Application of the ARL Model 72000 X-ray Quantometer to the Analysis of Steel," Reprint from Applied Research Laboratories, Sunland, Calif. (1968).

77. D. F. Sermin, "The Application of the ARL 72000 X-ray Quantometer to the Analysis of Stainless Steel," Reprint from Applied Research Laboratories, Sunland, Calif. (1969).

78. D. F. Sermin and K. Slickers, "The Application of the ARL Model 72000 X-ray Quantometer to the Analysis of Aluminum Base Alloys," Reprint from Applied Research Laboratories, Sunland, Calif. (1968).

79. D. F. Sermin and P. Roy, "The Application of the ARL 72000 X-ray Quantometer to the Analysis of Copper Base Alloys," Reprint from Applied Research Laboratories, Sunland, Calif. (1969).

Organometallics (Also see papers in section: Oil)

80. S. A. Bartkiewicz and E. A. Hammatt, "X-ray Fluorescence Determination of Cobalt, Zinc and Iron in Organic Matrices," Anal. Chem. 36, 833 (1964).

81. K. P. Champion and R. N. Whittem, "The Determination of Calcium in Biological Samples by X-ray Fluorescence," Analyst 92, 112 (1967).

82. G. V. Alexander, "An X-ray Fluorescence Method for the Determination of Calcium, Potassium, Chlorine, Sulfur, and Phosphorus in Biological Tissues," Anal. Chem. 37, 1671 (1965).

Slurry Streams, and Feeds and Sediments in Flotation Processes

83. P. J. Dunton, "Determination of Total Bromine in Brines by X-ray Fluorescence," Appl. Spectrosc. 22, 99 (1968).

84. A. H. Smallbone and E. Davidson, "Determination of Low Z Number Elements in Oils, Slurries and Solutions," Reprint from Applied Research Laboratories, Sunland, Calif. (1972).

85. A. H. Smallbone, "New X-ray Fluorescence Analytical Techniques and Material Handling Methods," Reprint from Applied Research Laboratories, Sunland, Calif. (1965).

86. A. H. Smallbone and E. Davidson, "On Stream Analysis of Solutions," Reprint from Applied Research Laboratories, Sunland, Calif. (1972).

87. A. H. Smallbone, "Liquid Cell (#128375) for X-ray Fluorescence Analysis," Reprint from Applied Research Laboratories, Sunland, Calif. (1970).

88. U. M. Cowgill, "Use of X-ray Emission Spectroscopy in the Chemical Analysis of Lake Sediments, Determining 41 Elements," Reprint from the author at the Dept. of Biology, Yale University (1968).

89. U. M. Cowgill, "Method to Determine All Detectable Exchangeable Cations Using X-ray Emission and Optical Emission Spectroscopy," Appl. Spectrosc. 22, 415 (1968).

90. K. J. Garska, "Microgram Determination of Chlorides by Deposition as Silver Chloride and X-ray Fluorescence," Anal. Chem. 40, 809 (1968).

91. W. A. Rowe and K. P. Yates, "X-ray Fluorescence Method for Trace Metals in Refinery Fluid Catalytic Cracking Feedstocks," Anal. Chem. 35, 368 (1963).

92. H. Hellman, "Determination of Metals in River Sludge by X-ray Fluorescence and Its Application in Actual Practice," Z. Anal. Chem. 254, 192 (1971). In German.

93. Y. K. Park, "Trace Element Determination in Natural Waters by X-ray Fluorescence Spectrometry after Concentration by Evaporation," Dachan Hwabak Hwoejee 13, 41 (1969). In Korean.

94. Y. K. Park, "Trace Element Determination in Natural Waters by X-ray Fluorescence Spectrometry After Continuous Dithizone Extraction in a Pulsed Column," Dachan Hwabak Hwoejee 13, 45 (1969). In Korean.

Slags and Glass

95. S. H. Laning, "X-ray Study of Glass," The Glass Industry Mar., 118 (1962).

96. D. F. Sermin and P. Roy, "The Application of the ARL 72000 X-ray Quantometer to the Analysis of Glass Powders," Reprint from Applied Research Laboratories, Sunland, Calif. (1969).

97. E. W. Orrell, "Ceramic Analysis by X-ray Fluorescence - the Non-Automatic Spectrometer," Br. Ceram. Res. Ass. Spec. Pub. 50, 70 (1966).

98. R. S. Lowe, "Ceramic Analysis by X-ray Fluorescence - the Automatic Instrument," Br. Ceram. Res. Ass. Spec. Pub. 50, 79 (1966).

99. F. H. Dörr, "Rontgenfluoreszenzanalytische Methoden für die Glasanalyse," Glastechn. Ber. 34, 175 (1961).

100. D. A. Stephenson, "Theoretical Analysis of Quantitative X-ray Emission Data: Glasses, Rocks and Metals," Anal. Chem. 43, 1761 (1971).

Applications of Electron Probe Microanalysis (X-ray Microprobe)

101. L. S. Birks and R. E. Seebold, "Use of the Electron Probe to Measure Low Average But High Local Concentrations," ASTM Spec. Tech. Pub. 308 (1961).

102. J. Philibert, "The Castaing Microsonde in Metallurgical and Mineralogical Research," J. Inst. Met. 90, 241 (1961).

103. J. Philibert and C. Crussard, "Applications of the Electron Probe Microanalyzer," J. of the Iron and Steel Inst. 183, 42 (1956).

104. R. J. Bird, "Electron Probe Micro-analysis in a Petroleum Research Laboratory," Inst. Petroleum 48, 297 (1962).

105. L. S. Birks and R. E. Seebold, "Diffusion of Nb with Cr, Fe, Ni, Mo and Stainless Steel," J. Nuclear Materials 3, 249 (1961).

106. L. S. Birks, J. M. Siomkjlo and P. K. Koh, "Identification of Chi and Sigma Phases in Stainless Steel with the Electron Probe Microanalyzer," AIME Transaction 218, 806 (1960).

107. E. J. Brooks and L. S. Birks, "Electron Probe Analysis of Segregation in Inconel," ASTM Spec. Tech. Pub. 245, 100 (1958).

108. K. C. Carroll, "Metallurgical Applications of the Electron Microprobe," J. Inst. Met. 91, 66 (1962).

109. R. Castaing, J. Philibert and C. Crussard, "Electron Probe Microanalyzer and its Application to Ferrous Metallurgy," J. of Metals 9, 389 (1957).

110. D. B. Clayton, T. B. Smith and J. R. Brown, "The Application of Electron Probe Microanalysis to the Study of Microsegregation in Low Alloy Steel," J. Inst. Met. 90, 224 (1961).

111. J. W. Colby, "Electron Microprobe Examination of Phosphides in Uranium," NLCO-870, Summary Technical Report, Jan. 1 to March 31, 1963, pp. 83-91, National Lead Company.

112. V. G. Macres, "Application of Electron Probe Microanalysis to Cu-Zn Diffusion," Thesis (MIT) 1958).

113. D. A. Melford and P. Duncumb, "The Metallographic Application of X-ray Scanning Microanalysis," Metallurgia 57, 159 (1958).

114. D. A. Melford and P. Duncumb, "The Application of X-ray Scanning Microanalysis to Some Metallurgical Problems," Metallurgia 61, 205 (1960).

115. L. S. Birks, E. J. Brooks, I. Adler and C. Milton, "Electron Probe Analysis of Minute Inclusions of a Copper-Iron Mineral," Am. Mineral 44, 974 (1959).

116. R. Castaing and K. Fredriksson, "Analyses of Cosmic Spherules with an X-ray Microanalyzer," Geochim. et Cosmochim. Acta 14, 114 (1958).

117. K. F. J. Heinrich, "Identification of Inclusions with the Electron Probe Microanalyzer," ASTM Spec. Tech. Pub. 393, 39 (1966).

118. A. K. Temple, K. F. J. Heinrich and J. F. Ficca, Jr., "Quantitative Electron Microprobe Analysis of Ilmenite Ores," in The Electron Microprobe, McKinley, Heinrich and Wittry, eds., Wiley, New York, p. 784 (1966).

119. K. F. J. Heinrich, "Electron Probe Microanalysis: A Review," Appl. Spectrosc. 22, 395 (1968).

Books Related to Electron Probe Microanalysis

120. T. D. McKinley, K. F. J. Heinrich, D. B. Wittry, eds., "The Electron Microprobe," Wiley, New York (1966).

121. K. F. J. Heinrich, "Quantitative Electron Probe Microanalysis," NBS Spec. Pub. 298, Washington, D. C. (Oct. 1968).

122. L. S. Birks, "Electron Probe Microanalysis," 2nd Ed., Wiley, New York (1971).

Supplemental References

123. H. E. Bumstead, "Application of the X-ray Spectrometer to the Needs of the Industrial Hygiene Laboratory," Indust. Hygiene J., p. 392 (1964.

124. J. W. Cares, "The Quantitative Determination of Airborne Metallic Dusts and Fumes by X-ray Spectrometry," Amer. Indust. Hygiene Assn. J., p. 463 (1968).

125. J. R. Rhodes, et al., "Energy Dispersive X-ray Analysis of Air Particulates in Texas," Environ. Sci. and Tech. 6, 922 (1972).

126. C. L. Luke, et al., "X-ray Spectrometric Analysis of Air Pollution Dust," Environ. Sci. and Tech. 6, 1105 (1972).

127. G. H. Heichel and L. Harkin, "Particulate Contaminates of Lead, Chlorine and Bromine Determined on Trees with an Electron Microprobe," Environ. Sci. and Tech. 6, 1121 (1972).

128. V. E. Cosslett, New York Academy of Science Annals 97, 464-481 (1962).

CHAPTER 5

ATOMIC ABSORPTION SPECTROMETRY

Theodore C. Rains

1. INTRODUCTION

Atomic absorption spectrometry (AAS) has been demonstrated to be a sensitive and selective technique for inorganic analysis (1-4). This technique is presently being used to determine the major, minor and trace elements in a wide variety of materials such as water, petroleum products, metals, ores, air particulates and biomedical materials. In atomic absorption methods of chemical analysis, a portion of the sample is converted into an atomic vapor, and the absorbance of light by this vapor is measured at a specific wavelength which is characteristic of the analyte. The unkown concentration is determined by comparison with absorbance measurements on standards of known composition.

The advantages of AAS may be summarized as (1) the large number of elements which can be determined with one instrument, (2) the low limits of detection, (3) the relative freedom from interferences, (4) the speed of analysis with no elaborate separations required, and (5) the absence of need for highly trained technical personnel for most types of AAS analysis.

2. INSTRUMENTATION AND TECHNIQUE

A wide range of AAS instruments for making accurate and precise measurements is commercially available. The basic components of an AAS instrument consist of a primary source of radiation, a means of producing atomic vapor, a wavelength isolator, radiation detector and readout system.

In general, hollow-cathode lamps are used as the primary source of radiation; they are available commercially for all elements which can be determined by AAS. As a rule they meet the basic requirements and are readily applicable to all AAS instruments.

The conventional means of producing atomic vapor of the analyte is to nebulize the sample solution into a flame. This is a wasteful and inefficient process but it is simple and convenient, and hence continues to be used. In recent years, nonflame sources have been used to produce atomic vapor (5). Examples of such devices include plasma torches, stabilized arcs and heated graphite furnaces. Of these three sources the heated graphite furnace has advantages over flame methods in greater sensitivity, lower detection limits, and the ability to accomodate very small samples (0.5 to 50 μl). The main factors in the production of atomic vapor are (a) efficiency of atomization, (b) length of flame or nonflame cell, (c) oxidant-fuel used to produce atomic vapor, and (d) position within atomic vapor in which absorption measurements are made.

Requirements for the wavelength selector may vary considerably from element to element. Basically, it is essential to be able to separate the one required spectral line from all others, and to keep any backgound intensity to a minimum. The means by which this is achieved may vary from a simple filter, in the case of sodium, to a high resolution monochromator with a band pass of 1 Å for the determination of nickel, iron and cobalt. If background radiation is emitted by the primary source of radiation, a narrow band pass in the selector will minimize its effect. There are some special instances where a narrow band pass is required to avoid interferences due to the selection of more than one absorption line.

To detect the radiation, a multiplier phototube with its associated power supply and measuring system are essential for high sensitivity and precision. Because the detection system is affected directly by the stability of the measuring circuit, the multiplier phototube, power supply, amplifier, and readout system must be sensitive and stable. At present, many types of multiplier phototubes and associated electronics are available commercially.

Seventy elements have been determined by AAS with detection limits in an aqueous media of 10 to 10^{-4} µg/ml. With non-flame methods such as the carbon rod atomizer, the detection limits for 33 of these elements have been extended to an absolute value of 10^{-11} to 10^{-14} grams, and this list of elements is growing almost daily.

A. Interferences

Interferences do occur in varying degrees for all elements determined by AAS. Interferences can be classified as physical or chemical (10). Physical interferences are effects which are caused by a physical property of the sample solution, or which alter one of the physical processes involved in the atomization process. Of all the physical interferences, light scattering by particles in the atomization process usually is the most troublesome. Techniques have been developed using background correctors but the analyst must be alert to the possibility of light scatter, especially for those elements emitting in the ultraviolet region of the spectrum, and apply the proper correcting technique.

Chemical interferences are classified as condensed phase, ionization, and mutual. Condensed phase interference occurs when a concomitant (element, radical, or solute present in solution) inhibits the dissociation or excitation of the analyte, thereby suppressing the signal. Ionization interference occurs when the analyte is ionized in the flame causing a reduction in signal strength. Mutual or interelement interference is not well understood but it has been observed, particularly in the nitrous oxide - acetylene flame, that the presence of a particular element may enhance or suppress the absorption due to an analyte.

To eliminate or control chemical interferences in AAS it is essential that the various instrumental parameters be optimized. These include type of burner, oxidant-fuel ratio, flame temperature, flame region, and sample. The flame or atomization temperature plays a major role in determining the extent of chemical interference. With the high temperature nitrous oxide - acetylene flame the chemical interference of aluminum, titanium, silicon, sulfate, or phosphate on the alkaline-earth metals is removed. However, this high-temperature flame usually introduces another type of interference which is caused by ionization of the analyte, but this can be controlled by the addition of a cation having a similar or lower ionization potential than that of the analyte.

Another way to eliminate condensed phase type of interference is by the addition of releasing or protective chelating agents. Releasing or protective chelating agents are defined as substances which, when added in sufficient quantity in the presence of an interferent, will restore the absorption of the analyte to its original value.

In some extreme cases liquid-liquid extraction is used to remove the interferent; this has an added effect of increasing the sensitivity of the analysis by preconcentrating the analyte.

3. SAMPLE REQUIREMENTS

The kinds of samples suitable for analysis by atomic absorption spectrometry cover a wide range. The analyte may be present in only trace quantities or it may be a major constituent. The type and quantity of sample being analyzed usually affect the selection of a sampling method and sample preparation. Trace analysis frequently requires special sampling and preparation techniques. Some factors which must be considered are (a) the sampling process, (b) procedures for obtaining samples in solution, and (c) methods of separation or preconcentration, if required. The nature of the sample matrix (e.g. coal, fly ash, ores, minerals, metals, etc.) governs the choice of sampling, dissolution, and preconcentration steps.

A. Sampling

A particular sampling approach which the analyst should follow is dictated by the concentration of the analyte and the specific purpose for the analysis. The sampling procedure or the lack of sample homogeneity have been known to introduce errors much greater than those associated with the chemical determinations. Calder (65) has shown that in the analysis of potassium in herbage, the variance due to sampling was ten times greater than the variance for the flame determinations.

B. Sample Preparation

The procedures for sample dissolution and subsequent treatment depend upon the sample matrices being analyzed; naturally, one method of sample treatment cannot be expected to work well for all matrices, and it is necessary to choose the best approach for any particular sample. A review of various techniques for the preparation of samples for AAS analysis has been made, which includes biochemical, agricultural, metallurgical, mining, geochemical, industrial, and other types of samples (5-7).

At the present state-of-the-art, solutions are normally required for atomic absorption spectrometry. A new technique using a carbon rod or furnace is currently being developed which holds promise that solid samples (e.g. fly ash, air particulates, etc.) may soon be analyzed directly; but the overwhelming majority of present-day AAS determinations is made on solutions.

Sample Dissolution

Samples with a high content of organic material respond well to dry ashing (heating for 2-4 hours at 500 °C) with subsequent dissolution of the residue in a mineral acid. If wet ashing is preferred, the sample may be heated with a mixture of nitric and perchloric acids, though other combinations of acids with sulfuric acid are preferred for some matrices. Most metals and alloys are soluble in hydrochloric and nitric acids. If silicates and the more refractory elements are present, the addition of hydrofluoric acid is essential. To dissolve the more refractory ores and minerals, the sample may be decomposed in a specially designed

Teflon vessel with hydrofluoric acid and a small quantity of aqua regia. The time required for decomposition is 30-40 min at a temperature of 110 °C.

It is important that the acids used for dissolving the samples be of such purity that they do not contribute trace elements of their own to the analytical results.

Separation or Preconcentration

Separation or preconcentration or both are frequently required as a part of AAS determination of trace elements. Separation methods, as distinct from preconcentration steps, are normally utilized to separate the analyte from the matrix or from other interfering species. Preconcentration steps are performed when the sensitivity or detection limits of the method are insufficient for the analysis. Due to the high specificity of AAS analyses, it is possible in most instances to perform a general, nonspecific separation and preconcentration step for one or several elements. The methods of separation and preconcentration are liquid-liquid extraction, ion exhange and coprecipitation. Of these three methods, liquid-liquid extraction is preferred and used extensively in atomic absorption spectrometry. Chelating agents most frequently used include 8-quinolinol (oxine), dithizone (diphenylthiocarbazone), cupferron, and several dithiocarbamate derivatives, particularly diethylammonium diethyldithiocarbamate and ammonium pyrrolidine dithiocarbamate (7).

The chelates formed are extracted into a water - immiscible, nonaqueous solvent such as methyl isobutyl ketone (MIBK). After removal of the aqueous phase, the metal-bearing organic phase is introduced into the flame and the absorption measured. This technique not only separates the analyte from the matrix, but also yields an increase in sensitivity due to the effect of the organic solvent on the flame.

4. APPLICATION TO MATERIALS OF ENVIRONMENTAL INTEREST

Atomic absorption spectrometry has been compared with other spectrochemical methods (8) and with other techniques of chemical analysis (9) for a variety of materials. In many laboratories AAS has supplanted wet chemical methods due to its specificity, low limits of detection, capability of determining many elements in one sample solution, freedom from elapsed-time requirements of those methods in which reactions must go to completion, and provision for data output in digital-concentration form.

In the past five years papers have been published describing AAS techniques for diverse environmentally impacting materials which include agricultural - fertilizer, plants, and soils; clinical - air, blood, tissue and hair, urine and bone; industrial - cement, chemicals, coal, gasoline and liquid fuels, lubricating oils, pharmaceuticals, and polymers; nutritional - beverages, fats and foodstuff; metallurgical - iron and steel, ferrous and non-ferrous alloys and refractory materials; <u>mining</u> and <u>geochemical</u> - minerals, ores, silicates and water samples. It appears that AAS has been used to analyze almost every known type of material.

5. RESULTS AND CONCLUSIONS

A. Tabulated Information

Tables 1-6 summarize the literature described in references 1-65. Detection limits, required sample sizes, and analytical costs are collected for the elements of interest at expected concentrations in the range 1, 10, and 100 ppm. At these levels the expected accuracy of AAS analyses is 25 percent, 15 percent, and 5 percent respectively. This contrasts with the instrumental precision of AAS analysis of 1-2 percent and analytical accuracy of better than 2 percent at macro concentration levels. The attainment of these expected levels of accuracy in the analyses depends on the continued use of reliable standards.

Stock solutions of standards are prepared from high purity metals which are available as NBS Standard Reference Materials (SRM's). Procedures for the preparation of 77 standard solutions are described by Dean and Rains (5). The quality of the standards used during the analytical measurements is of great importance in trace element determinations.

Column 10 in Tables 1-6 is an element index to the references, and provides entry to additional information on individual elements in specific matrices. No literature was available on the determination of fluorine and thorium by atomic absorption spectrometry.

B. Costs

No great operator skill or experience are needed to operate AAS instruments, and less operational dexterity is required with flame methods than with most other types of spectroscopic sources. However, training in the observation of possible causes of error is essential for trace element determinations. Hazards to the operator are few, but proper safety precautions must be learned and practiced, especially when using nitrous oxide - acetylene flames.

Atomic absorption spectrometers are relatively inexpensive, with a price range of $3,500 to $12,000. The estimated analytical costs may be expected to decrease from the values listed in the tables, as the number of elements to be determined in the same solution is increased. Atomic absorption spectrometry appears to be capable of providing an analytical capability which can meet the financial requirements of most industrial and municipal laboratories.

C. Conclusions

Atomic absorption spectrometry is a versatile analytical tool which can be used to determine 25 of 27 elements of interest present in macro or trace concentrations as constituents in environmentally significant matrices. Its high specificity, moderate instrument and labor requirements, and simple operating procedure make it eminently suited for routine trace element determinations at a reasonable cost.

Table 1. Analysis of Metals and Alloys by Atomic Absorption Spectrometry Flame Method

Element	Expected Conc'n. (ppm)	Accuracy (%)	Eqpt. Req'd. (a)	Time to Prepare Sample (hr)	Sample Size (g)	Detection Limit (μg/g)	Cost[(f)] Per Analysis ($)	Com-ments	References
Hg	1,10,100	25,15,5	A	2-4	1-5	1	50-100		38,53
Be	"	"	B	2-4	0.1-1	0.3	40-60	(b)	6,7,14
Cd	"	"	C	2-4	.01-.1	0.1	20-40	(b)	6,7,14,62
As	"	"	D	2-4	0.1-1	0.2	20-40	(b,e)	7,14,44
V	"	"	B	2	0.1-1	0.2	20-40	(b)	7,14,22,19
Mn	"	"	C	2-4	0.1-1	0.1	40-60		6,7,14,19
Ni	"	"	C	2	0.1-1	0.1	20-40	(b)	6,7,14,19
Sb	"	"	C	2-4	0.1-1	0.1	40-60	(b)	14,22,61
Cr	"	"	C	2	0.1-1	0.5	20-40	(b)	6,7,14,19
Zn	"	"	C	2	0.1-1	0.1	20-40	(b)	19,22,62
Cu	"	"	C	2	0.1-1	0.2	20-40	(b)	7,19,22,41
Pb	"	"	C	2	0.1-1	0.1	20-40	(b)	7,22,41,61
Se	"	"	C	2-4	0.1-1	0.2	40-60	(b)	7,22,54
B	10,100	15,5	B	2-4	1-5	10	50-100		7
F	No information.								
Li	1,10,100	25,15,5	C	2	0.1-1	0.01	20-40		6,7,19,22
Ag	"	"	C	2	0.1-1	0.1	20-40	(b)	7,19,22,41
Sn	"	"	C	2-4	0.1-1	0.1	40-60	(b)	43,61
Fe	"	"	C	2	0.1-1	0.1	20-40	(b)	6,7,19,22
Sr	"	"	C	2	0.1-1	0.1	20-40	(c)	7,22,56
Na	"	"	C	2	0.01-.1	0.01	20-40		6,7,22,56
K	"	"	C	2	0.01-.1	0.01	20-40		6,7,22,56
Ca	"	"	B	2	0.1-1	0.1	20-40	(c,d)	7,19,22
Si	10,100	15,5	B	4-6	1-5	1	40-60		7,22
Mg	1,10,100	25,15,5	C	2	0.1-1	0.1	20-40	(d)	6,7,19,22
U	10,100	15,5	B	2-4	1-5	10	50-100		7
Th	No information.								

(a) AAS, plus oxidants and fuels: A=Ar+H_2; B=$N_2O+C_2H_2$; C=Air+C_2H_2; D=Air+H_2.
(b) Separation and preconcentration required for 1 ppm.
(c) Releasing agent required ($LaCl_3$).
(d) Ionization suppressor required.
(e) Molecular scatter.
(f) Costs include nontechnical personnel skilled in AAS analyses.

Table 2. Analysis of Fly Ash, Ores and Minerals by Atomic Absorption Spectrometry Flame Methods

Element	Expected Conc'n. (ppm)	Accuracy (%)	Eqpt. Req'd. (a)	Time to Prepare Sample (hr)	Sample Size (g)	Detection Limit (μg/g)	Cost[(e)] Per Analysis ($)	Com-ments	References
Hg	1,10,100	25,15,5	A	2-4	1-5	1	50-100		6,53
Be	"	"	B	2-4	0.1-1	0.5	50-100		19,41,49
Cd	"	"	C	2-4	0.01-1	0.1	40-60	(b)	22,41,50,51
As	"	"	A	2-4	0.1-1	0.2	40-60	(b)	44,47,51
V	"	"	B	2-4	0.1-1	0.6	40-60		22,51
Mn	"	"	C	2-4	0.1-1	0.1	40-60		22,51
Ni	"	"	C	2-4	0.1-1	0.1	40-60	(b)	25,27,41
Sb	"	"	A	2-4	0.1-1	0.1	40-60	(b)	6,7,22
Cr	"	"	B	2-4	0.1-1	0.5	40-60		6,7,19,51
Zn	"	"	C	2-4	0.1-1	0.1	40-60	(b)	22,23,45,50,59
Cu	"	"	C	2-4	0.1-1	0.2	40-60	(b)	22,41,51
Pb	"	"	C	2-4	0.1-1	0.2	40-60	(b)	22,23,41
Se	"	"	A	2-4	0.1-1	0.2	40-60	(b)	22,47,54
B	10,100	15,5	B	2-6	1-5	10	50-100		48
F	No information.								
Li	1,10,100	25,15,5	C	2-4	0.01-1	.01	40-60		7,22,56
Ag	"	"	C	2-4	0.1-1	0.2	40-60	(b)	22,23,41
Sn	"	"	A	2-4	1-5	1	50-100	(b)	22,50
Fe	"	"	C	2-4	0.1-1	0.1	40-60		7,22,45,56
Sr	"	"	C	2-4	0.1-1	0.1	40-60	(c)	22,45
Na	1,10,100	25,15,5	C	2-4	0.01-.1	.01	40-60		7,27
K	"	"	C	2-4	.01-.1	.01	40-60		27,46
Ca	"	"	B	2-4	0.1-1	.1	40-60	(d)	6,27,46,51
Si	10,100	15,5	B	2-6	1-5	1	50-100		7,22,46
Mg	1,10,100	25,15,5	C	2-4	0.1-1	.1	40-60	(c)	7,27,45,46
U	10,100	15,5	B	2-4	1-5	10	40-60		7
Th	No information.								

(a) AAS, plus oxidants and fuels: A=Ar+H_2; B=N_2O+C_2H_2; C=Air-C_2H_2.
(b) Separation and preconcentration required for 1 ppm.
(c) Releasing agent required ($LaCl_3$).
(d) Ionization suppressor required.
(e) Costs include nontechnical personnel skilled in AAS analyses.

Table 3. Analysis of Fly Ash, Ores, Minerals, Metals and Alloys by Atomic Absorption Spectrometry Non-Flame Methods

Element	Expected Conc'n. (ppm)	Accuracy (%)	Eqpt. Req'd (a)	Time to Prepare Sample (hr)	Sample Size (g)	Detection Limit (μg/g)(c)	Cost(b) Per Analysis ($)	Com-ments	References
Hg	1,10,100	25,15,5	A	2-4	0.001-0.1	10^{-4}	40-60	(d)	37,39,40,53
Be	"	"	B	2-4	0.001-0.1	10^{-6}	40-60	(d)	5,26,33
Cd	"	"	B or C	2-4	0.001-0.1	10^{-8}	40-60	(d)	33,39,60
As	"	"	C	2-4	0.001-0.1	10^{-4}	40-60	(d)	39,60,63
V	"	"	C	2-4	0.001-0.1	10^{-3}	40-60	(d)	36,60,63
Mn	"	"	B or C	2-4	0.001-0.1	10^{-6}	40-60	(d)	33,34,36,60
Ni	"	"	B or C	2-4	0.001-0.1	10^{-5}	40-60	(d)	33,34,36,60
Sb	"	"	B or C	2-4	0.001-0.1	10^{-5}	40-60	(d)	60,63
Cr	"	"	B or C	2-4	0.001-0.1	10^{-5}	40-60	(d)	34,60,63
Zn	"	"	B or C	2-4	0.001-0.1	10^{-6}	40-60	(d)	5,36,60,63
Cu	"	"	B or C	2-4	0.001-0.1	10^{-6}	40-60	(d)	5,36,60,63
Pb	"	"	B or C	2-4	0.001-0.1	10^{-5}	40-60	(d)	33,34,36,60
Se	"	"	B or C	2-4	0.001-0.1	10^{-4}	40-60	(d)	35,39,60,63
B	"	"	B	2-4	0.001-0.1	10^{-3}	40-60	(d)	36,60
F	No information.								
Li	"	"	B or C	2-4	0.001-0.1	10^{-4}	40-60	(d)	5,60
Ag	"	"	B or C	2-4	0.001-0.1	10^{-7}	40-60	(d)	34,36,39,60
Sn	"	"	B or C	2-4	0.001-0.1	10^{-5}	40-60	(d)	60
Fe	"	"	B or C	2-4	0.001-0.1	10^{-5}	40-60	(d)	33,60,63
Sr	"	"	B or C	2-4	0.001-0.1	10^{-5}	40-60	(d)	36,57,60,63
Na	"	"	B or C	2-4	0.001-0.1	10^{-4}	40-60	(d)	60,63
K	"	"	B or C	2-4	0.001-0.1	10^{-4}	40-60	(d)	5
Ca	"	"	B or C	2-4	0.001-0.1	10^{-5}	40-60	(d)	39,60,63
Si	"	"	B	2-4	0.001-0.1	10^{-6}	40-60	(d)	36,60,63
Mg	"	"	B or C	2-4	0.001-0.1	10^{-6}	40-60	(d)	33,60,63
U	No information.								
Th	No information.								

(a) AAS plus A = cold vapor method; B = carbon furnace; C = tantalum ribbon.
(b) Costs include nontechnical personnel skilled in AAS analyses.
(c) Separation and preconcentration required.
(d) Molecular scatter, background correction required.

Table 4. Analysis of Slurry Streams and Process Streams by Atomic Absorption Spectrometry Flame Methods

Element	Expected Conc'n. (ppm)	Accuracy (%)	Eqpt. Req'd (a)	Time to Prepare Sample (hr)	Sample Size (g)	Detection Limit (μg/g)	Cost(b) Per Analysis ($)	Com- ments	References
Hg	1,10,100	25,15,5	A	2-4	1-5	1	50-100		53
Be	"	"	B	2-4	0.1-1	0.5	50-100	(c)	7,49,55
Cd	"	"	C	2-4	0.01-1	0.1	50-100	(c)	50,55
As	"	"	D	2-4	0.1-1	0.2	50-100	(c)	7,55
V	"	"	B	2-4	0.1-1	0.6	50-100	(c)	7,55
Mn	"	"	C	2-4	0.1-1	0.1	50-100		24,27
Ni	"	"	C	2-4	0.1-1	0.1	50-100	(c)	7,27
Sb	"	"	A	2-4	0.1-1	0.1	50-100	(c)	7,24
Cr	"	"	B	2-4	0.1-1	0.5	50-100	(c)	24,27
Zn	"	"	C	2-4	0.1-1	0.1	50-100	(c)	24,27,50
Cu	"	"	C	2-4	0.1-1	0.2	50-100	(c)	24,27
Pb	"	"	C	2-4	0.1-1	0.2	50-100	(c)	24,27,55
Se	"	"	A	2-4	0.1-1	0.2	50-100	(c)	54
B	10,100	15,5	B	2-6	1-5	10	50-100		48,55
F	No information.								
Li	1,10,100	25,15,5	C	2-4	0.01-1	0.01	50-100		7
Ag	"	"	C	2-4	0.1-1	0.2	50-100	(c)	55
Sn	"	"	A	2-4	1-5	1	50-100	(c)	24,50
Fe	"	"	C	2-4	0.1-1	0.1	50-100	(c)	24,27
Sr	"	"	C	2-4	0.1-1	0.1	50-100	(c)	55
Na	"	"	C	2-4	0.01-.1	0.01	50-100		7
K	"	"	C	2-4	.01-.1	0.01	50-100		7
Ca	"	"	B	2-4	0.1-1	0.1	50-100	(d)	7
Si	10,100	15,5	B	2-4	1-5	1	50-100		7
Mg	1,10,100	25,15,5	C	2-4	0.1-1	0.1	50-100	(e)	55
U	10,100	15,5	B	2-4	1-5	10	50-100		7
Th	No information.								

(a) AAS plus oxidants and fuels: $A=Ar+H_2$; $B=N_2O+C_2H_2$; $C=Air+C_2H_2$; $D=Air+H_2$.
(b) Costs include nontechnical personnel skilled in AAS analyses.
(c) Separation and preconcentration required for 1 ppm.
(d) Ionization suppressor required.
(e) Releasing agent required ($LaCl_3$).

Table 5. Analysis of Coal, Oil, Organometallics by Atomic Absorption Spectrometry Flame Methods

Element	Expected Conc'n. (ppm)	Accuracy (%)	Eqpt. Req'd (a)	Time to Prepare Sample (hr)	Sample Size (g)	Detection Limit (µg/g)	Cost[(b)] Per Analysis ($)	Com-ments	References
Hg	1,10,100	25,15,5	A	2	1-5	1	20-40		6,38,53
Be	"	"	B	2-4	0.1-1	0.3	40-60	(c)	6,11
Cd	"	"	C	2	0.01-1	0.1	20-40	(c)	6,35
As	"	"	A	2-4	0.1-1	0.2	20-40	(c)	12,13,47
V	"	"	B	2	0.1-1	0.6	20-40	(d)	6,14
Mn	"	"	C	2	0.1-1	0.1	20-40	(d)	6,14,17,38
Ni	"	"	C	2	0.1-1	0.1	20-40	(d)	6,14,16,39
Sb	"	"	A	2	0.1-1	0.1	20-40	(c)	15
Cr	"	"	B	2-4	0.1-1	0.5	20-40	(d)	6,19,28,31
Zn	"	"	C	2	0.1-1	0.1	20-40	(d)	6,20,35
Cu	"	"	C	2	0.1-1	0.2	20-40	(c)	28,31,32,35
Pb	"	"	C	2	0.1-1	0.5	20-40	(c)	28,32,35
Se	"	"	A	2-4	0.1-1	0.2	20-40	(c)	13,47
B	10,100	15,5	B	2-4	1-5	10	50-100		11,19,48
F	No information.								
Li	1,10,100	25,15,5	C	2	0.1-1	0.01	20-40		6,20,45
Ag	"	"	C	2	0.1-1	0.3	20-40	(e)	20,21,31,32
Sn	10,100	"	D	2-4	1-5	1	40-60		6,28
Fe	1,10,100	"	C	2	0.1-1	0.1	20-40		19,28,31,32
Sr	"	"	C	2	0.1-1	0.1	20-40	(f)	6,7,56
Na	"	"	C	2	0.01-.1	0.1	20-40		6,19,28
K	"	"	C	2	0.01-.1	.05	20-40		6,7,56,64
Ca	"	"	C	2	0.1-1	0.1	20-40	(f)	38,58,64
Si	10,100	"	B	4-6	1-5	1	50-100		6,20,28,42
Mg	1,10,100	"	C	2	0.1-1	0.1	20-40	(f)	6,20,21,64
U	10,100	"	B	2-4	1-5	10	50-100		7
Th	No information.								

(a) AAS plus oxidants and fuel: A=Ar+H_2; B=N_2O+C_2H_2; C=Air+C_2H_2; D=Air+H_2.

(b) Costsinclude nontechnical personnel skilled in AAS analyses.

(c) Separation and preconcentration required for 1 ppm.

(d) Ionization suppressor required.

(e) Molecular scatter interferences.

(f) Releasing agent required ($LaCl_3$).

Table 6. Analysis of Coal, Oil and Organometallics by Atomic Absorption Spectrometry Non-Flame Methods

Element	Expected Conc'n. (ppm)	Accuracy (%)	Eqpt. Req'd (a)	Time to Prepare Sample (hr)	Sample Size (g)	Detection Limit (μg/g)	Cost[b] Per Analysis ($)	Com-ments	References
Hg	1,10,100	25,15,5	A	2-4	.001-0.1	10^{-4}	40-60	(c,d)	18,37,39,40, 52,53
Be	"	"	B	"	"	10^{-6}	"	"	60,63
Cd	"	"	B or C	"	"	10^{-8}	"		39,63
As	"	"	C	"	"	10^{-4}	"	"	47,60,63
V	"	"	C	"	"	10^{-3}	"	"	36,63
Mn	"	"	B or C	"	"	10^{-6}	"	"	5,60,63
Ni	"	"	B or C	"	"	10^{-5}	"	"	18,60,63
Sb	"	"	B or C	"	"	10^{-5}	"	"	60,63
Cr	"	"	B or C	"	"	10^{-5}	"	"	60,63
Zn	"	"	B or C	"	"	10^{-6}	"	"	39,60,63
Cu	"	"	B or C	"	"	10^{-6}	"	"	18,60,63
Pb	"	"	B or C	"	"	10^{-5}	"	"	18,39,63
Se	"	"	B or C	"	"	10^{-4}	"	"	5,39,47
B	"	"	B or C	"	"	10^{-3}	"	"	60
F	No information.								
Li	1,10,100	25,15,5	B or C	"	"	10^{-4}	"	"	5,60
As	"	"	B or C	"	"	10^{-7}	"	"	5,18,63
Sn	"	"	B or C	"	"	10^{-5}	"	"	60
Fe	"	"	B or C	"	"	10^{-5}	"	"	5,18,36
Sr	"	"	B or C	"	"	10^{-5}	"	"	60
Na	"	"	B or C	"	"	10^{-4}	"	"	5
K	"	"	B or C	"	"	10^{-4}	"	"	5
Ca	"	"	B or C	"	"	10^{-5}	"	"	5,39,63
Si	"	"	B	"	"	10^{-6}	"	"	36,63
Mg	"	"	B or C	"	"	10^{-6}	"	"	5,18,19,63
U	No information.								
Th	No information.								

(a) AAS plus: A=cold vapor method; B=carbon furnace; C-tantalum ribbon furnace.
(b) Costs include nontechnical personnel skilled in AAS analyses.
(c) Separation and preconcentration required to attain stated detection limits.
(d) Molecular scatter, background correction required.

References

1. Hubbard, D. P., "Annual Reports on Analytical Atomic Spectroscopy," Volume 1, Society for Analytical Chemistry, London, 1972.

2. Winefordner, J. D. and Vickers, T. J., Flame Spectrometry, Anal. Chem. 44, 150R (1972).

3. Slavin, W., "Atomic Absorption Spectroscopy," Interscience, New York, 1968.

4. David, D. J., The Application of Atomic Absorption to Chemical Analysis, Analyst 85, 779 (1960).

5. Dean, J. A., and Rains, T. C., Editors, "Flame Emission and Atomic Absorption Spectrometry," Volume 2, Components and Techniques, Marcel Dekker, New York, 1971.

6. Slavin, W., Atomic-Absorption Spectroscopy-Critical Review, Appl. Spectrosc. 20, 281 (1966).

7. Mavrodineanu, R., Editor, "Analytical Flame Spectroscopy, Selected Topics," Macmillan, London, 1970.

8. Grant, C. L., A Comparison of Atomic Absorption with Other Spectrochemical Methods, in "Atomic Absorption Spectroscopy," ASTM STP 443, American Society for Testing and Materials, Philadelphia, 1969, pp. 37-46.

9. Lewis, L. L., A Comparison of Atomic Absorption with Some Other Techniques of Chemical Analysis, in "Atomic Absorption Spectroscopy," ASTM STP 443, American Society for Testing and Materials, Philadelphia, 1969, pp. 47-69.

10. Dean, J. A., and Rains, T. C., Editors, "Flame Emission and Atomic Absorption Spectrometry," Volume 1, Theory, Marcel Dekker, New York, 1969.

11. Chakrabarti, C. L., Beryllium, Boron, Aluminun, Gallium, Indium, and Thallium, Chapter in "Flame Emission and Atomic Absorption Spectrometry," J. A. Dean and T. C. Rains, Editors, Volume 3, Marcel Dekker, New York, in press.

12. Fernandez, F. J., and Manning, D. C., The Determination of Arsenic at Sub-Microgram Levels by Atomic Absorption Spectrophotometry, At. Abs. Newsl. 10, 86 (1971).

13. Manning, D. C., A High Sensitivity Arsenic-Selenium Sampling System for Atomic Absorption Spectroscopy, At. Abs. Newsl. 10, 123 (1971).

14. Slavin, S., Barnett, W. B., and Kahn, H. L., The Determination of Atomic Absorption Detection Limits by Direct Measurement, At. Abs. Newsl. 11, 37 (1972).

15. Pollock, E. N., and West, S. J., The Determination of Antimony at Submicrogram Levels by Atomic Absorption Spectrophotometry, At. Abs. Newsl. 11, 104 (1972).

16. Keyworth, D. A., Petroleum Products, Chapter in "Flame Emission and Atomic Absorption Spectrometry," J. A. Dean and T. C. Rains, Editors, Volume 3, Marcel Dekker, New York, in press.

17. Bartels, T. T., and Wilson, C. E., Determination of Methyl Cyclopentadienyl Manganese Tricarbonyl in JP-4 Fuel by Atomic Absorption Spectrophotometry, At. Abs. Newsl. 8, 3 (1969).

18. O'Gorman, J. V., Suhr, N. H., and Walker, P. L., Jr., The Determination of Mercury in Some American Coals, Appl. Spectrosc. 26, 44 (1972).

19. Christian, G. D., and Feldman, F. J., A Comparison Study of Detection Limits Using Flame-Emission Spectroscopy with the Nitrous Oxide-Acetylene Flame and Atomic-Absorption Spectroscopy, Appl. Spectrosc. 25, 660 (1971).

20. Oliver, M., The Determination of Trace Metals in Polymers by Atomic Absorption Spectrophotometry, At. Abs. Newsl. 10, 12 (1971).

21. Barnett, W. B., Hahn, H. L., and Peterson, G. F., The Rapid Determination of Several Elements in a Single Lubricating Oil Sample by Atomic Absorption Spectroscopy, At. Abs. Newsl. 10, 106 (1971).

22. "Analytical Methods for Atomic Absorption Spectrometry," Perkin-Elmer Corp., Norwalk, Conn., 1968.

23. Thomas, B. G., Determination of Silver, Lead, and Zinc in High Grade Ores, At. Abs. Newsl. 10, 73 (1971).

24. Price, J. P., Utilization of Atomic Absorption Spectroscopy in the Synthetic Fiber Industry, At. Abs. Newsl. 11, 1 (1972).

25. Stresko, V., and Martiny, E., Determination of Antimony in Geological Materials by Atomic Absorption Spectrometry, At. Abs. Newsl. 11, 4 (1972).

26. Sighinolfi, G. P., Determination of Beryllium in Standard Rock Samples by Flameless Atomic Absorption Spectroscopy, At. Abs. Newsl. 11, 96 (1972).

27. Fleming, H. D., Some Applications of Atomic Absorption Spectroscopy in Metallurgical Laboratories, Atomic Absorption Spectroscopy Symposium, May, 1970, Melbourne, Australia (Published by Varian Techtron Pty. Ltd., Australis).

28. Sanders, J. B., Application to the Analysis of Petroleum Products, ibid.

29. Dagnall, R. M., and West, T. S., Observations on the Atomic Absorption Spectroscopy of Lead in Aqueous Solutions in Organic Extracts and In Gasoline, Talanta 11, 1553 (1964).

30. Mostyn, R. A., and Cunningham, A. F., Some Applications of Atomic Absorption Spectroscopy to the Analysis of Fuels and Lubricants, J. Inst. Petrol. 53, 101 (1967).

31. Burrows, J. A., Heedt, J. C., and Willis, J. B., Determination of Wear Metals in Used Lubricating Oils by Atomic Absorption Spectrophotometry, Anal. Chem. 37, 579 (1965).

32. Moore, E. J., Milner, O. I., and Glass, J. R., Application of Atomic Absorption Spectroscopy to Trace Analyses of Petroleum, Microchem. J. 10, 148 (1966).

33. Moffith, A. E., Quinn, P. M., and Limtiaco, L. P., Applications of Atomic Absorption Spectrophotometry in Occupational Health Studies, Amer. Lab., p. 8 (August 1971).

34. Kahn, H. L., Graphite Furnace Applications in Atomic Absorption, Amer. Lab., p. 35 (August 1971).

35. Bazhov, A. S., Zherebenko, A. V., and Koko, P. A., Atomic Absorption Analysis of Polymetallic Ores, J. Anal. Chem. of USSR 26, 1485 (1971).

36. Amos, M. D., Nonflame Atomization in AAS - A Current Review, Amer. Lab., p. 57 (August 1972).

37. Rains, T. C., and Menis, O., Determination of Submicrogram Amounts of Mercury in Standard Reference Materials by Flameless Atomic Absorption Spectrometry, JAOAC 55, 1339 (1972).

38. Eider, N. G., Determination of Metals in Paint and Vinyl Additives by Atomic Absorption Spectrometry, Appl. Spectrosc. 25, 313 (1971).

39. Gandrud, B. W., and Skogerboe, R. K., Investigation of the Hollow Cathode Discharge as an Atomic Absorption Medium, Appl. Spectrosc. 25, 243 (1971).

40. Goleb, J. A., The Determination of Mercury in Small Terrestrial and Nonterrestrial Rock Samples by Atomic Absorption Spectroscopy, and the Study of Mercury Release at Elevated Temperatures, Appl. Spectrosc. 25, 522 (1971).

41. Sackdev, S. L., and West, P. W., Concentration of Trace Metals by Solvent Extraction and their Determination by Atomic-Absorption Spectrophotometry, Environ. Sci. Technol. 4, 749 (1970).

42. Prey, V., Teichmann, H., and Bickler, D., Die Bestimmung von Silicium in Organischen Verbindungen mit Hilfe der Atomarabsorption, Mikrochim. Acta, 138 (1970).

43. Headridge, J. B. and Sowerbutts, A., The Determination of Tin in Steel by Solvent Extraction Followed by Atomic Absorption Spectrophotometry, Analyst 97, 442 (1972).

44. Menis, O., and Rains, T. C., Determination of Arsenic by Atomic Absorption Spectrometry with an Electrodeless Discharge Lamp as a Source of Radiation, Anal. Chem. 41, 952 (1969).

45. Abbey, S., Analysis of Rocks and Minerals by Atomic Absorption Spectroscopy, I, Determination of Magnesium, Lithium, Zinc, and Iron, Canada Depart. of Energy, Mines Resources, Geol. Survey of Canada, Paper No. 67-37, 1967.

46. Abbey, S., Analysis of Rocks and Minerals by Atomic Absorption Spectroscopy, II, Determination of Total Iron, Magnesium, Calcium, Sodium, and Potassium, Canada Dept. of Energy, Mines Resources, Geol. Survey of Canada, Paper 68-20, 1968.

47. Kirkbright, G. F., Sargent, M., and West, T. S., The Determination of Arsenic and Selenium by Atomic Absorption Spectroscopy in a Nitrogen-Separated-Air Acetylene Flame, At. Abs. Newsl. 8, 34 (1969).

48. Harris, R., Determination of Small Quantities of Boron by Atomic Absorption Spectrophotometry, At. Abs. Newsl. 8, 42 (1969).

49. Peterson, Y. A., Determination of Beryllium in Aluminum Materials by Atomic Absorption Spectrophotometry, At. Abs. Newsl. 8, 53 (1969).

50. McCracken, J. D., Vecchione, M. C., and Longo, S. L., Ion Exchange Separation of Traces of Tin, Cadmium, and Zinc From Copper and Their Determination by Atomic Absorption Spectrophotometry, At. Abs. Newsl. 8, 102 (1969).

51. Thompson, R. J., Morgan, G. B., and Purdue, L. J., Analysis of Selected Elements in Atmospheric Particulate Matter by Atomic Absorption, At. Abs. Newsl. 9, 53 (1970).

52. Kalb, G. W., The Determination of Mercury in Water and Sediment Samples by Flameless Atomic Absorption, At. Abs. Newsl. 9, 84 (1970).

53. Manning, D. C., Non-Flame Methods for Mercury Determination by Atomic Absorption - A Review, At. Abs. Newsl. 9, 97 (1970).

54. Nakahara, T., Munemori, M., and Muska, S., Determination of Selenium in Sulfur by Atomic Absorption Spectrophotometry, Anal. Chim. Acta 50, 51 (1970).

55. Kopp, J. F., and Kroner, R. C., "Trace Metals in Waters of the United States," U. S. Dept. of Interior, F.W.P.C.A., Division of Pollution Surveillance, Cincinnati, Ohio, 1967.

56. Rains, T. C., Chemical Aspects of Atomic Absorption, in "Atomic Absorption Spectroscopy," ASTM STP 443, American Society for Testing and Materials, Philadelphia, 1969, pp. 19-36.

57. Belcher, C. B., and Brooks, K. A., The Determination of Strontium in Coal Ash by Atomic Absorption Spectrophotometry, Anal. Chim. Acta 29, 202 (1963).

58. Kashiki, M., and Oshima, S., Universal Standard Method for Atomic Absorption Spectroscopy of Organic Materials, Bunseki Kagaku 20, 1398 (1971).

59. Allan, R. E., Pierce, J. O., and Yeager, D., Determination of Zinc in Food, Urine, Air, and Dust by Atomic Absorption, Amer. Ind. Hygiene Assoc. J. 29, 469 (1968).

60. Kirkbright, G. F., The Application of Non-flame Cells in Atomic-absorption and Atomic-fluorescence Spectroscopy, Analyst 96, 609 (1971).

61. Burke, K. E., Non-Aqueous Atomic Absorption Spectroscopy Determination of Microgram Quantities of Antimony, Bismuth, Lead, and Tin in Aluminum, Iron, and Nickel-Base Alloys, Paper number 30, presented at Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, February 28-March 5, 1971.

62. Kuroha, T., Tsukahara, I., and Shibuya, S., Determination of Microamounts of Cadmium, and Zinc in Copper, Nickel, Aluminum and Uranium Metals by Solvent Extraction - Atomic Absorption Spectrophotometry, Japan Analyst 20, 1137 (1971).

63. Hwang, J. Y., Trace Metals in Atmospheric Particulates and Atomic Absorption Spectroscopy, Anal. Chem. 44, No. 14, 20A (1972).

64. Obermiller, E. L., and Freedman, R. W., Rapid Determination of Calcium, Magnesium, Sodium, Potassium and Iron in Coal Ash by Atomic Absorption Spectrophotometry, Fuel 44, 199 (1965).

65. Calder, A. B., The Statistical Approach in Analytical Chemistry: Why it is Important, Anal. Chem. 36, No. 9, 25A (1964).

CHAPTER 6

ABSORPTION SPECTROPHOTOMETRY

R. W. Burke

1. INTRODUCTION

For the past forty years, absorption spectrophotometry has played a major role in the analysis of important industrial and research materials. Numerous factors have been responsible for the popularity of this technique. Foremost among these are: (1) its modest apparatus requirements, (2) the possibility of its use by skilled technicians, (3) its good sensitivity and (4) its high accuracy.

Several points should be clearly understood, however, before discussing specific applications of this technique to the analysis of the wide variety of materials which are currently of interest to EPA. First, absorption spectrophotometry is, for all practical purposes, a wet-chemical technique. Samples must therefore always be dissolved before an analysis can be made. Depending on the type and complexity of the matrix, sample dissolution can be, and frequently is, the limiting step in the analytical procedure. This deficiency, however, is common to all wet-chemical techniques and is best overcome by the analyst's experience. A second drawback of absorption spectrophotometry is that it is primarily a single element technique. Consequently, it is not suited for quick, survey-type, analyses. Finally, the technique is generally not specific and, as a rule, its successful application requires that the element of interest be separated from the remainder of the matrix. Such a requirement may be considered both a weakness and a stength. For example, separations may be tedious and small losses of the desired constituent may occur. Also, interfering elements may not be completely eliminated. On the other hand, if satisfactory separations can be made - and this is more often true than not - the effect of foreign elements is eliminated, and the spectrophotometric method becomes essentially an absolute one. This is often not the case with more sophisticated instrumental techniques in which chemical separations generally are not made. The accuracy of the latter methods depends on the availability of well characterized standards whose compositions closely approximate that of the materials being analyzed. In absorption spectrophotometry, suitable standards are prepared from high purity elements or compounds which are readily available commercially.

2. ANALYSIS OF SPECIFIC MATERIALS

Tables 1 and 2 summarize the relevant information on the possible spectrophotometric determination of some twenty-one elements in fly ash, incinerator particulates, coal, oil, ores, minerals, metals, alloys, organometallics, slurry streams and flotation feeds. Most of the references cited are not matrix oriented, but instead, deal specifically with the isolation, preconcentration and spectrophotometric determination of a particular element. This approach was necessary for two reasons: (1) there are relatively few references in the literature dealing with the spectrophotometric analyses of the above matrices and (2) those that were found employed for the most part, at least from the viewpoint of the research analyst, inferior methods. These findings are not surprising however, since widespread interest in the analysis of these types of materials has arisen only in the past few years. The lack of procedures is undoubtedly further accentuated by the fact that absorption spectrophotometry is primarily a single element rather than a survey technique.

The criteria used to divide the various matrices into the two general groups given in Tables 1 and 2 were (1) their complexity and (2) their ease of dissolution. It is these same two factors which dictate the differences in accuracy and detection limits listed. Further examination of the two tables will show that a number of elements have been marked with an asterisk. These are the elements which are considered best determined by absorption spectrophotometry.

Perhaps the most variable parameters in these tables relate to the time and cost of an analysis. The figures given were taken largely from personal experience and are the best estimates for a "one-shot," single element determination. These costs can undoubtedly be substantially reduced, perhaps even tenfold, by determining several elements on the same sample and/or by determining the same element simultaneously in a number of samples of similar material.

As already mentioned, one of the advantages of absorption spectrophotometry is its modest apparatus requirement. This is indeed true since, for about $5,000, a laboratory can become well equipped to analyze for most of the elements listed. In spite of its relatively low cost, spectrophotometric instrumentation is quite rugged with downtime perhaps averaging no more than 1 percent.

3. CONCLUSIONS

The primary purpose of this chapter has been the delineation of state-of-the-art procedures for the spectrophotometric determination of some twenty-one elements in fly ash, incinerator particulates, coal, oil, ores, minerals, metals, alloys, organometallics, slurry streams and flotation feeds.

The majority of the references cited deal with the fundamental chemistry involved in the selective separation and color-forming reactions of these elements. By employing highly selective separations, the accuracy of the measurement should be scarcely affected by the nature of the matrix being analyzed, provided adequate dissolution procedures are used.

In all of the methods referred to above, solvent extraction has invariably been the method of choice when separations are necessary. This method is the most widely used technique because of its simplicity and speed. By utilizing apparatus no more complicated than a separatory funnel and requiring at most a few minutes to perform, solvent extraction offers a superior approach to performing elemental analyses of these types of materials. They are especially useful in absorption spectrophotometry since separation, preconcentration, and, frequently, color development can be performed in the same operation.

The greatest impact that absorption spectrophotometry can make in the near future appears to be in the areas of standards development and analysis. However, once more definitive specifications and tolerances are established, spectrophotometry should play an important role in the quality control and routine analysis of these materials.

Spectrophotometric procedures have been heavily automated in the clinical field, and commercially available auto-analyzers are highly popular. This suggests strongly that the same can be done for industrial applications, with attendant savings in costs and convenience for routine trace element determinations of the future.

Table 1. Analysis of Coal, Oil, Organometallics, Metals, and Alloys by Absorption Spectrophotometry[a]

Element[b]	Expected Conc'n. (ppm)	Accuracy (%)	Sample Size (g)	Expected Conc'n. (ppm)	Accuracy (%)	Sample Size (g)	Detection Limit[c] (μg)	Inter-ferences	References
Hg	1-10	25	1.0	100	5	0.1	0.1	Cu, Ag	1-5
Be*				1-100	5	0.1	0.1		6,7
Cd*	1-10	15	1.0	100	5	0.1	0.1	Co	8
As*	1-10	25	1-2	100	5	0.1	0.5		1A,9,10
V				10-100	15	1-2	5		1B,2B,11
Mn*	1-10	25	1-2	100	5	0.1	5		12,13
Ni*	1-10	5	1-2	100	5	1.0	0.1	Cu, Co	3B,14,15
Sb*				1-100	5	0.1-0.5	0.1	Au, Tl	16,17
Cr	1-10	25	1-2	100	5	0.1	0.5		18
Zn	1-10	15	1.0	100	5	0.1	0.1		2A,3A,19,20
Cu*				1-100	5	0.1	0.1	Hg, Pd	3B,21,22
Pb	1-10	15	1.0	100	5	0.1	0.1		4B,23
Se*				1-100	15	0.1	0.1	Mo, V	24,25,26
B*	1-10	15	1.0	100	5	0.1	0.1		27-33
F				10-100	15	1.0	2		4A,34,35,36
Ag	1-10	15	1.0	100	5	0.1	0.5		37,38
Sn*	1-10	25	1-2	100	5	0.1	1		39,40,41,42
Fe*	1-10	15	1.0	100	5	0.1	0.1		6B,43,44
Si*	1-10	25	2-5	100	5	0.5	0.5		45,46
U				10-100	15	1.0	2		47,48,49
Th				10-100	15	1.0	2		50,51

(a) Precision u.v.-visible spectrophotometer; skilled technician requires 0.5 - 4 hours for sample preparation; cost $50 - 100 per sample.

(b) Method recommended particularly for elements marked with an asterisk; not recommended for determination of Li, Sr, Na, K, Ca, Mg.

(c) To convert μg to ppm divide the detection limits (μg) by the sample weights (g).

Table 2. Analysis of Fly Ash, Ores, Minerals, Incinerator Particulates, Slurry Streams, Process Feeds by Absorption Spectrophotometry[(a)]

Element[(b)]	Expected Conc'n. (ppm)	Accuracy (%)	Sample Size (g)	Expected Conc'n. (ppm)	Accuracy (%)	Sample Size (g)	Detection Limit[(c)] (μg)	Inter-ferences	References
Hg	10	25	1.0	100	5	0.1	2	Cu, Ag	1-5
Be*	1-10	25	1.0	100	5	0.1	0.5		1C,6,7
Cd*	10	15	1.0	100	5	0.1	1	Co	8
As*	1-10	25	1-2	100	5	0.1	0.5		1C,9,10
V	10	25	1-5	100	5	1-5	5		11
Mn*	10	25	1.0	100	5	0.1	5		12,13
Ni*	1-10	25	1.0	100	5	0.1	0.5	Cu, Co	14,15
Sb*	1-10	25	1-2	100	5	0.1	0.5	Au, Tl	16,17
Cr	10	25	1-5	100	5	1-5	2		18
Zn	10	25	1-2	100	5	1-2	2		19,20
Cu*	1-10	25	1.0	100	5	0.1	0.5	Hg, Pd	21,22
Pb	10	25	1.0	100	5	0.1	2		23
Se*	1-10	25	1.0	100	5	0.1	0.5	Mo, V	3C,24,25,26
B*	10	25	1.0	100	5	0.1	2		27-33
F	--	--	--	10-100	25	1	2		34,35,36
Ag	10	25	1.0	100	5	0.1	2		37,38
Sn*	10	25	1-2	100	5	0.5	2		39-42
Fe*	10	25	1.0	100	5	0.1	1		43,44
Si*	1-10	25	2-5	100	5	0.5	0.5		45,46
U				10-100	25	1-2	5		47,48,49
Th				10-100	25	1-2	5		50,51

(a) Precision u.v.-visible spectrophotometer; skilled technician requires 2-8 hours for sample preparation; cost $100-200 per sample.

(b) Method recommended particularly for elements marked with an asterisk; not recommended for determination of Li, Sr, Na, K, Ca, Mg.

(c) To convert μg to ppm divide the detection limits (μg) by the sample weights (g).

References

1. Committee Report, The Determination of Small Amounts of Mercury in Organic Matter, Analyst 90, 515 (1965).

2. Smart, N. A., and Hill, A. R. C., Determination of Mercury Residues in Potatoes, Grain and Animal Tissues Using Perchloric Acid Digestion, Analyst 94, 143 (1969).

3. Toribara, T. Y., Shields, C. P., and Koval, L., Behavior of Dilute Solutions of Mercury, Talanta 17, 1025 (1970).

4. Miller, W. L., and Wachter, L. E., Determination of Traces of Mercury in Copper Alloys, Anal. Chem. 22, 1312 (1950).

5. Sandell, E. B., "Colorimetric Determination of Traces of Metals," 3rd ed., pp. 621-630, Interscience, New York, 1959.

6. Adam, J. A., Booth, E., and Strickland, J. D. H., The Determination of Microgram Amounts of Beryllium Using Acetyl Acetone, Anal. Chim. Acta 6, 462 (1952).

7. Kirkbright, G. F., West, T. S., and Woodward, C., Spectrofluorometric Determination of Submicrogram Amounts of Aluminum and Beryllium with 2-Hydroxy-3-naphthoic Acid, Anal. Chem. 37, 137 (1965).

8. Sandell, E. B., "Colorimetric Determination of Traces of Metals," 3rd ed., pp. 350-365, Interscience, New York, 1959.

9. NBS Tech. Note 424, "Analytical Coordination Chemistry: Titrimetry, Gravimetry, Flame Photometry, Spectrophotometry, and Gas Evolution, July 1966 to June 1967," Menis, O., Editor, pp. 64-67 (1968).

10. Nall, W. R., An Improved Method for the Determination of Arsenic in Steel, Analyst 96, 398 (1971)

11. Stary, J., Systematic Study of the Solvent Extraction of Metal Oxinates, Anal. Chim. Acta 28, 132 (1963).

12. Motojima, K., Hashitani, H., and Imanashi, T., Spectrophotometric Determination of Microgram Quantities of Manganese in Uranium and Aluminum with 8-Hydroxyquinaldine, Anal. Chem. 34, 571 (1962).

13. Sandell, E. B., "Colorimetric Determination of Traces of Metals," 3rd ed., pp. 606-620, Interscience, New York, 1959.

14. Stary, J., "The Solvent Extraction of Metal Chelates," p. 189, MacMillan Company, New York, 1964.

15. Burke, R. W., and Deardorff, E. R., Simultaneous Spectrophotometric Determination of Cobalt, Nickel and Copper with 2,3-Quinoxalinedithiol, Talanta 17, 255 (1970).

16. Burke, R. W., and Menis, O., Extraction-Spectrophotometric Determination of Antimony as a Ternary Complex, Anal. Chem. 38, 1719 (1966).

17. Fogg, A. G., Jillings, J., Marriott, D. R., and Burns, D. T., A Critical Study of Brilliant Green as a Spectrophotometric Reagent: The Determination of Antimony, Analyst 94, 768 (1969).

18. Sandell, E. B., "Colorimetric Determination of Traces of Metals," 3rd ed., pp. 388-397, Interscience, New York, 1959.

19. Margerum, D. W., and Santacana, F., Evaluation of Methods for Trace Zinc Determination, Anal. Chem. 32, 1157 (1960).

20. Stary, J., and Ruzicka, J., Isotopic Dilution Analysis by Solvent Extraction, Talanta 8, 296 (1961).

21. Stary, J., "The Solvent Extraction of Metal Chelates," p. 164, MacMillan Company, New York, 1964.

22. Bailey, B. W., Dagnall, R. M., and West, T. S., Analytical Applications of Ternary Complexes-II. Spectrophotometric Determination of Copper as Rose Bengal Bisphenanthrolinium Copper (II), Talanta 13, 753 (1966).

23. Sandell, E. B., "Colorimetric Determination of Traces of Metals," 3rd ed., pp. 555-583, Interscience, New York (1959).

24. Hoste, J., and Gillis, J., Spectrophotometric Determination of Traces of Selenium with Diaminobenzidine, Anal. Chim. Acta 12, 158 (1955).

25. Cheng, K., Determination of Traces of Selenium, Anal. Chem. 28, 1738 (1956).

26. Kawashima, T., and Tanaka, M., Determination of Submicrogram Amounts of Selenium(IV) by Means of the Catalytic Reduction of 1,4,6,11-Tetraazanaphthacene, Anal. Chim. Acta 40, 137 (1968).

27. Spicer, G. S., and Strickland, J. D. H., The Determination of Microgram and Sub-microgram Amounts of Boron, Anal. Chim. Acta 18, 231 (1958).

28. Freegarde, M., and Cartwright, J., The Determination of Boron in Zircaloy, Analyst 87, 214 (1962).

29. Hayes, M. R., and Metcalfe, J., The Boron-Curcumin Complex in the Determination of Trace Amounts of Boron, Analyst 87, 956 (1962).

30. Uppström, L. R., A Modified Method for Determination of Boron with Curcumin and a Simplified Water Elimination Procedure, Anal. Chim. Acta 43, 475 (1968).

31. Dyrssen, D. W., Novkov, Y. P., and Uppström, L. R., Studies on the Chemistry of the Determination of Boron with Curcumin, Anal. Chim. Acta 60, 139 (1972).

32. Babko, A. K., and Marchenko, P. V., Photometric Determination of Boron in Steel, Zavod. Lab. 26, 1202 (1960).

33. Marcantonatoes, A., and Monnier, D., Study of Several New Fluorescent Reactions of Boric Acid and Fluorimetric Determination of Nanogram Quantities of Boron (in French), Helv. Chim. Acta 48, 194 (1965).

34. Belcher, R., Leonard, M. A., and West, T. S., A New Spot Test for the Detection of Fluoride Ion, Talanta 2, 92 (1959).

35. Bartkiewicz, S. A., and Robinson, J. W., Rapid Method for the Determination of Fluoride in Liquids, Anal. Chim. Acta 22, 427 (1960).

36. Belcher, R., and West, T. S., A Study of the Cerium(III)-Alizarin Complexan-Fluoride Reaction, Talanta 8, 853 (1961).

37. Dagnall, R. M., and West, T. S., A Selective and Sensitive Colour Reaction for Silver, Talanta 11, 1533 (1964).

38. El-Ghamry, M. T., and Frei, R. W., Spectrophotometric Determination of Trace Amounts of Silver(I), Anal. Chem. 40, 1986 (1968).

39. Ross, W. J., and White, J. C., Application of Pyrocatechol Violet as a Colorimetric Reagent for Tin, Anal. Chem. 33, 424 (1961).

40. Dagnall, R. M., West, T. S., and Young, P., The Catechol Violet Colour Reaction for Tin(IV) Sensitised by Cetyltrimethylammonium Bromide, Analyst 92, 27 (1967).

41. Smith, J. D., The Spectrophotometric Determination of Microgram Amounts of Tin with Phenylfluorone, Analyst 95, 347 (1970).

42. Busev, A. I., Shestidesyatnaya, N. L., and Zimomrya, G. G., Extraction of Tin(II) as its Compound with Brilliant Green, Zh. Anal. Khim. 26, 1517 (1971).

43. Moore, F. L., Fairman, W. D., Ganchoff, J. G., and Surak, J. G., Selective Liquid-Liquid Extraction of Iron with 2-Thenoyltrifluoroacetone-Xylene, Anal. Chem. 31, 1148 (1959).

44. Diehl, H., and Smith, G. F., "The Iron Reagents," 2nd ed., G. Frederick Smith Chemical Company, Columbus, Ohio (1965).

45. Ringbom, A., Ahlers, P. E., and Sütonen, S., The Photometric Determination of Silicon as α-Silicomolybdic Acid, Anal. Chim. Acta 20, 78 (1959).

46. Halasz, A., Pungor, E., Properties and Analytical Applications of the Heteropolymolybdates of Phosphorus, Arsenic, Silicon and Germanium, Talanta 18, 557 (1971).

47. Stary, J., and Hladky, E., Systematic Study of the Solvent Extraction of Metal β-Diketonates, Anal. Chim. Acta 28, 227 (1963).

48. Florence, T. M., and Farrar, Y., Spectrophotometric Determination of Uranium with 4-(2-Pyridylazo)resorcinol, Anal. Chem. 35, 1613 (1963).

49. Burke, R. W., Exchange Reactions of Ternary Ion-Association Complexes Directly in the Organic Phase, Talanta 17, 240 (1970).

50. Meinke, W. W., and Anderson, R. E., Method for Continuous Extraction with a Chelating Agent, Anal. Chem. 24, 708 (1952).

51. Sandell, E. B., "Colorimetric Determination of Traces of Metals," 3rd ed., pp. 844-851, Interscience, New York, 1959.

Coal

1A. Abernethy, R. F., and Gibson, F. H., Colorimetric Method for Arsenic in Coal, U. S. Bur. Mines Rep. Invest. 7184 (1968).

2A. Anand, K. S., Dayal, P., and Anand, O. N., Determination of Zinc in Lubricating Oils and Lubricating Oil Concentrates, Z. Anal. Chem. 239, 33 (1968).

3A. Weaver, C., The Determination of Zinc in Coal, Fuel 46, 407 (1967).

4A. Abernethy, R. F., and Gibson, F. H., Method for Determination of Fluorine in Coal, U. S. Bur. of Mines Rep. Invest. 7054 (1967).

Oil

1B. Macmillan, E., and Samuel, B. W., Spectrophotometric Determination of Low Concentrations of Vanadium in Petroleum with Hematoxylin, Anal. Chem. 38, 250 (1966).

2B. Steinke, I., Photometric Determination of Vanadium in Oil Fractions (in German), Z. Anal. Chem. 233, 265 (1968).

3B. Scoggins, M. W., Ultraviolet Spectrophotometric Determination of Nickel, Anal. Chem. 42, 301 (1970).

4B. Lambdin, C. E., and Taylor, W. D., Determination of Trace Copper in Petroleum Middle Distillates with Cuprizone, Anal. Chem. 40, 2196 (1968).

5B. Campbell, K., and Moss, R., Determination of Trace Amounts of Lead in Crude Oil and Petroleum Products, J. Inst. Petrol. 53, 194 (1967).

6B. Short, F. R., Eyster, C. H., and Scribner, W. G., Spectrophotometric Determination of Parts-Per-Billion Iron in High-Temperature Hydrocarbon Jet Fuels, Anal. Chem. 39, 251 (1967).

Particulates

1C. Sommer, L., and Kuban, V., Spectrophotometric Determination of Beryllium with Chrome Azurol S, Anal. Chim. Acta 44, 333 (1969).

2C. Stara, V., and Stary, J., Spectrophotometric Determination of Traces of Arsenic, Talanta 17, 341 (1970).

3C. Dickey, D. W., Wiersma, J. H., Barnekow, R. G., Jr., and Lott, P. F., Determination of Selenium by the Ring Oven Technique, Mikrochim. Acta 605 (1969).

CHAPTER 7

ATOMIC EMISSION SPECTROSCOPY

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1. INTRODUCTION

Atomic emission spectra of the elements have long provided a powerful means for multi-element, chemical trace analysis. The capabilities of optical emission spectrometric analysis have improved with the increasing demands of our developing technological age and the growing awareness of the contribution of trace concentrations of many elements to environmental contamination.

A modern perspective of the state-of-the-art for trace and sub-trace analysis by optical emission spectrometry (OES) can be obtained from several books (1B-6B) and reviews (1R-8R) on the subject. However, neither state-of-the-art nor details of techniques are simple to elucidate concisely. This chapter summarizes the most recent techniques for OES analysis for 27 elements in the matrices: fly ash, coal, oil, ores, minerals, metals, alloys, organometallics, incinerator particles, slurry streams, and feeds and sediments in flotation processes.

A. Optical Emission Sources

The basic sensitivity (change in analyte signal per unit change in analyte concentration) of optical emission spectrometry is a complex function of analyte element, sample matrix, emission source, detector(s), and spectrometer optics. Thus, elements that have low excitation potentials for resonance lines and little tendency to form stable or non-volatile compounds are readily detected and have good sensitivity in most plasma-like discharges. The importance of compound formation and volatility are most dramatically incurred with the classical direct-current arc discharge.

DC Arc

The common d-c arc customarily is described as a source more sensitive, but less precise, than spark-type electrical discharges (with electrode configurations: rotating disk, porous cup, vacuum cup, etc.). However, detectability of elements in solid and powdered matrices is more a function of the large (10-20 mg) undiluted (usually only slightly diluted with graphite or buffers) sample quantity that is vaporized into the arc discharge rather than inherent sensitivity for all elements. Typical detection limits for elements in silicate ores (non-volatile matrix) are listed in Table 1, column 1 (1). Spectroscopic buffers that control volatilization of solid compounds and stabilize excitation conditions in the arc plasma enable considerable improvement in spectrographic detectability. Harvey (2) has provided tabulated empirical data that show the importance of matrix and buffers. Harvey's detection limits for elements in a Li-salt buffer are shown in Table 1, column 2.

Further improvements in detectability of the elements in spectra from d-c arcs have come from the use of rare-gas atmospheres (usually Ar) that enclose the discharge (3, 4, 5, 6, 7). Atmospheres of argon, or argon mixed with a reactive gas (such as oxygen), have made possible the improved detectability illustrated in Table 1, column 3.

Most recently, Gordon and Chapman (8) have reported on a controlled-atmosphere, d-c arc method that uses AgCl as a common matrix. Their method, which is similar to residue methods discussed later in this chapter, requires a solution of the sample, but enables automated analyses for μg-quantities of analytes with good precision. Minimum detectable quantities (8) for elements of interest are illustrated in Table 1, column 4. Hambidge (9) adapted Gordon's method for analysis of chromium in blood, hair and urine. Serum aliquots of 0.2 ml provided 1-7 ng quantities of chromium that could be determined with coefficients of variation of about 6 percent.

Sparks and AC Arcs

Discharges characterized as high-voltage sparks and interrupted arcs generally provide means for measurements more precise than d-c arcs. However, solutions or residues from solutions are required. Solutions assure homogeneity and a convenient means for addition of internal references not common to d-c arc powder methods. Some typical detection limits by porous cup and rotating disk spark methods are given in Table 1, column 5 (10-13a, 13b).

Dilute solutions are particularly amenable to analysis by the copper-spark or graphite-spark technique. This method was first described by Gerlach and Riedl (14) in 1934, and later examined thoroughly by Fred, Nachtrieb and Tomkins (15) [for more recent descriptions, see references 16, 17, 18]. A residue is produced on flat-surfaced impermeable electrodes by vaporization of a small volume of solution. This residue then is sampled directly by a spark discharge. The method is sensitive and capable of high precision (1-3 percent). Typical minimum detectable quantities are shown in Table 1, column 6. The presence of large amounts of matrix material in the residue is detrimental to detectability and precision, however, chemical separations, such as extraction, ion exchange, or electrodeposition, possibly can be used to remove matrix elements and enrich (or preconcentrate) impurity elements of interest.

Duffendack et al. (19, 20) have utilized a high-voltage a-c arc, rather than a spark, for analysis of residues on graphite electrodes. High sensitivity and good accuracy (19, 21) have been shown for this technique. More recently, Zhigalovskaya et al. (22, also see 22a, 22b) have described a short-pulse d-c technique that they found superior to the copper spark method in determining nanogram quantities of elements.

Hollow Cathode

Mention also must be made of the hollow-cathode discharge. The hollow cathode provides intense line spectra of the elements and enables analysis of small samples. In addition, the source makes possible convenient analyses for the halogens and other elements with high excitation potentials. The method is essentially a residue technique because solid sample is placed or electrodeposited within the hollow cathode. Some typical absolute detection limits (23, also see 23a, 23b) are given in Table 1, column 7. Matrix effects are frequently incurred with this source, especially if the sampling mechanism is not ion sputtering alone. The hollow cathode lamp has been successfully applied to the analysis of trace elements in steels (23c) and non-conducting materials (23d)

Flame Emission

Flame atomic emission spectrometry is an important analytical technique that too frequently is overlooked in searches for analytical methods. Nearly 70 elements can be determined with flames that are in common use: nitrous oxide-acetylene, oxygen-acetylene, oxygen-hydrogen, etc. Some detection limits from oxygen-acetylene flames (24) are surveyed in Table 1, column 8.

From among the various micro-wave discharges, capacitative-coupled and inductively coupled flame-like plasmas, the induction-coupled argon plasma appears to be a source that provides stable, bright spectra and thus, good detectability for many elements. Table 1, column 9 summarizes detection limits from this source (25, 26).

B. Chemical Preconcentration

The key to OES analysis of many elements approaching part-per-billion concentrations is preconcentration (or enrichment) of impurities. General methodology and precautions have been described by Thiers (27), Minczewski (28), Mizuike (29), and Lighty and Currier (30).

The techniques of most importance to removal of impurities from a matrix and concentration are liquid-liquid extraction, ion-exchange and electrodeposition. Some typical details and commentary on application of these approaches to optical emission spectrometry have been given by Lighty (30) and others (16, 27).

Recently, Jackwerth et al. have described DTPA complex exchange reactions (30a), coprecipitation of trace elements with thallium iodide, followed by extraction with DDTC (30b), enrichment of copper as the copper-cuprizone complex on silver bromide (30c), and trace enrichment by partial dissolution of matrices (30d) as sample manipulations preceding spectrochemical analysis.

2. APPLICATION TO MATERIALS OF ENVIRONMENTAL INTEREST

The twelve matrices, subjects of this report, can be separated into five groups for discussion. These groups, which assemble similar matrices, are:

A. Group 1 - Streams to and from Air Scrubbers

The liquids and solids collected in wet scrubbers can be analyzed by techniques long established by Kopp and Kroner (31a, 31b, 32a, 33a, p. 1010). Kopp and Kroner analyzed for Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mo, Mn, Ni, P, Pb, Sr, V, and Zn in preconcentrated water samples by the rotating-disk high-voltage spark method. Concentrations from 0.01 to 100 μg/ml were determined on a direct-reading spectrometer. A volume of water evaporated (8 to 10 hrs) to 5 ml contained 20g of total solids/liter; the major portions of solids were salts of Ca, K, Mg, and Na. Concentration ranges for the various elements analyzed are shown in Table 2, column 1. Four other methods are discussed in the paper (31a). These techniques and others (31c, 31d), for spectrometric water analysis should be directly applicable to analysis of water from wet scrubbers.

Haffty (32b) has described a residue method capable of detecting almost 60 elements in the ng/ml range. The technique has been applied to analysis of water sediments. Barnett (33a, p.1001) has described a residue method for analysis of water. Concentration ranges are shown in Table 2, column 2. The method is accurate (5-15 percent) and has a 1-2 percent coefficient of variation.

B. Group 2 - Metals and Alloys (Fe, Al, Cu, Pb, Zn)

Methods for spectrometric analysis of the metals Al, Cu, Fe, Pb and Zn are detailed in the ASTM Methods for Emission

Spectrochemical Analysis (33a). Only metal constituents important to bulk metallurgical properties of these alloys are of concern in the ASTM methods. An example of elements and their concentration ranges determined in aluminum by the sensitive point-to-plane spark is given in Table 2, column 3. These concentration ranges typify the concentrations of interest for analysis of alloys of copper (33a, p. 445), of iron (33a, p. 215), of lead (33a, p. 490), and of zinc (33a, p. 532). Balfour, et al. (33b) have developed a chemical preconcentration technique that enables emission spectrochemical analysis to be carried out for parts-per-million of Ag, As, Au, Bi, Cd, Ge, In, Mo, Pb, Sn and Tl in alloys of Al, Cr, Co, Fe, Ni and Ti. Killeen (33c) has used a dc-arc for analysis of trace elements in aluminum.

Tymchuck, et al. (34a, 34b) have found that Cu(OH)F is a good carrier for analysis of trace impurities, from volatile arsenic to refractory vanadium, in high-purity copper. For ppm and sub-ppm determinations, chemical preconcentration methods, defined by the specific problem, will be required.

Elwell and Scholes (35), Dozinel (36), Tölle (36a) and Publicover (36b) provide further information on spectrometric analysis for traces and minor constituents in copper and its alloys. (See Table 2, column 5) Four alloy steels are treated in a special technical publication of the British Iron and Steel Institute (37). Thornton (23c) has analyzed for traces in several iron-base alloys with a hollow-cathode lamp. Atwell and Golden (37a) have developed a carrier-distillation method for analysis of Pb, Bi and Sn in nickel-base alloys.

C. Group 3 - Ores, Minerals, and Sediments from Coal Flotation Processes

Typical standard methods for spectrochemical analysis of ores, rocks, and minerals (33a, p. 267, p. 958, p. 968, p. 982, p. 1027) are concerned with major constituents. Simultaneous multiple-element analyses for trace elements in minerals and rocks have been treated by Avni and Boukobza (48), Tennant and Sewell (49), Moal et al. (50), Schoenfeld (51), de Villiers et al. (52) and in ores by DeMontleau (53). Shapiro (38a) recently has reviewed methodology for silicate rock analysis. Table 2, column 7 presents typical analyses of minerals.

Direct analysis of trace elements in ores can be accomplished with a buffer or with a carrier distillation method (34, 38). Also, there is an indication that boiler cap electrodes can provide improved d-c arc analysis for volatile elements, such as Hg, As and Zn (39, p. 239). Solution techniques for numerous ores require preliminary fusion with sodium peroxide or lithium metaborate. Collins (40) has analyzed waste waters from oil fields for B, Be, Fe, Mn and Sr by direct optical emission spectrography with a plasma-arc source.

D. Group 4 - Coal, Feeds to Coal Flotation Processes, Organometallics (formed by Combustion Processes)

The general subject of coal analysis for industry has been treated by Abernethy et al. (41a, 41b). Sharkey (42) has determined 53 elements in coal. Gibson and Ode (43) describe rapid methods for analysis of coal ash and similar matrices. Prior to solution of samples, a lithium metaborate fusion of the coal is accomplished in a platinum vessel (44, 45). Usual analytes and concentration ranges in the ashed residue are summarized in Table 2, column 4 (43).

E. Group 5 - Fly Ash and Incinerator Particles

Principal constituents of fly ash are Si, Fe and Mg. This matrix is amenable to direct d-c arc analysis; or,after suitable fusion with lithium tetraborate or hydrofluoric acid dissolution, analysis can be performed with a rotating disk technique. Fusions with lithium borate flux have been used to reduce sample matrix effects (46, 47). Automated methods similar to those described by Tennard and Sewell (49c) for silicate minerals may be applicable to fly ash and incinerator particles.

3. COST (TIME) OF ANALYSIS

A. Survey Analyses

Qualitative and semiquantitative analyses can be made for all elements that have resonance lines or other relatively intense spectral lines within the limits of photographic plate response and transmission characteristics of the optics external to the spectrograph. A conventional d-c arc qualitative analysis provides an identification of major, minor, and trace constituents (up to 70 elements) typically in 10 mg of solid sample. Qualitative analyses also can be performed on liquid samples directly by spark methods or indirectly by residue methods. A semiquantitative analysis provides additional information on concentrations in terms of decade ranges defined by available standards and photographic exposures measured on a scanning microphotometer. This type of analysis is usually limited to 40 or 45 elements in a specific matrix material.

The cost for survey analysis is a composite sum of time (man-hours), and costs of electrodes, reference standards, buffers, gases for special discharge atmospheres, photographic plates and reagents. The time required for an analysis is the most significant of these cost contributors. Estimated times for qualitative and semiquantitative analyses are reviewed in Table 4 for single sample multiple-element cases, and for multiple-sample multiple-element cases. All time estimates include the routine analysis; however, special samples may require up to several hours of pretreatment. The time required depends ultimately on the nature of the analysis and the complexity of the sample.

B. Quantitative Analyses

Quantitative analysis provides concentration information for traces and minor constituents that is typically accurate to within ± 5-10 percent of the true value. Reference standards such as the NBS Standard Reference Materials (SRM's) are necessary, and the physical and chemical similarity of standards and samples are crucial to the achievement of high accuracy.

Spectrographic methods require time-consuming microphotometry and graphical extrapolation methods. However, direct-reading (photoelectric) spectrometers can minimize or eliminate either or both of these time-consuming operations, thereby greatly reducing the time for quantitative measurements. These differences are reflected in the estimated times (costs) for quantitative analyses summarized in Table 4.

Table 1. Summary of Spectrographic and Spectrometric Detection Limits[a]

Element	DC Arc Air (ppm)	DC Arc Li-Salt Buffer (ppm)	DC Arc Controlled Atmosphere (ppm)	DC Arc Reduced Pressure Argon (ng)	Porous Cup & Rotating Disk (ppm)	Spark Copper & Graphite (ng)	Hollow Cathode (ng)	Flame (µg/ml)	Argon Induction-Coupled Plasma (ng/ml)
Hg	3000	70	0.3	—	10	10	—	40	200
Be	1	1.5	0.005	0.1	0.02	0.2	0.03	1	—
Cd	10	15	0.08	20	0.2	20	30	6	30
As	100	800	0.1	—	3	100	—	50	100
V	1	0.8	5	—	0.2	1	—	0.3	6
Mn	1	0.6	0.03	1	0.02	0.2	0.03	0.1	—
Ni	30	3	0.1	3	0.5	1	1	0.6	6
Sb	100	80	0.1	2	2	10	100	20	200
Cr	3	0.5	0.5	2	0.1	1	1	0.1	1
Zn	100	70	0.1	45	4	10	3	50	9
Cu	0.3	0.2	0.1	0.4	0.05	0.5	0.03	0.1	—
Pb	1	7	0.3	1	4	5	10	3	8
Se	—	—	500[b]	—	—	—	—	—	30
B	30	15	0.4	—	0.5	0.2	1	30	30
F	300	—	—	—	—	10	—	—	—
Li	30	20	500[b]	1	0.1	0.2	0.1	0.000003	—
Ag	0.1	0.8	0.001	—	0.01	0.5	0.03	0.3	20
Sn	3	15	0.1	7	2	—	10	4	300
Fe	30	5	0.4	0.3	0.2	2.5	3	0.7	5
Sr	3	0.2	5[b]	—	0.06	50	—	0.004	0.02
Na	100	20	500[b]	7	35[b]	10	0.03	0.0001	—
K	2000	15	1000[b]	20	200[b]	10	10	0.003	—
Ca	1	0.1	0.01	—	0.01	10	—	0.005	—
Si	3	8	0.4	3	1	10	1	5	—
Mg	0.3	0.2	0.1	0.2	0.003	1	0.03	0.2	5
U	50	500	500	—	100	100	—	10	30
Th	100	50	500	—	10	50	—	150	3

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[a] Index to references in Table 3.

[b] Most sensitive line not used.

Table 2. Summary of Spectrographic and Spectrometric Analysis of Various Materials[a]

Element	Water Rotating Disk Method (μg/ml)	Water Residue Method (μg/ml)	Aluminum Spark-Emission (%)	Coal Ash (Major Constituents)[b] (%)	Copper, Globular Arc (ppm)	Minerals, Phosphate Rock (ppm)	Minerals, Powders (ppm)
Hg	—	—	—	—	0.3-3	10-400	—
Be	0.005-1.4	0.6-30	0.001-1	—	0.01-0.2	10-400	1-6
Cd	0.2-20	6-30	0.001-2	—	0.1-1	10-400	5-6
As	4-80	—	—	—	3-40	10-400	1-2
V	2-40	1.5-30	0.001-0.05	—	0.1-1.5	10-400	20-90
Mn	0.1-20	1.5-3,000	0.001-8	—	0.1-0.8	10-400	200-1500
Ni	0.5-40	1.5-30	0.001-10	—	2-40	10-400	1-2500
Sb	—	—	—	—	2-40	10-400	0.6-1.2
Cr	0.2-40	1.5-30	0.001-4	—	0.2-3	10-400	8-400
Zn	0.5-80	90-3,000	0.001-10	—	0.5-10	10-400	40-700
Cu	0.2-40	0.3-300	0.001-30	—	—	10-400	13-8000
Pb	2-40	1.5-30	0.002-0.7	—	1-15	10-400	6-460
Se	—	—	—	—	—	—	—
B	0.1-20	1.5-300	0.001-0.05	—	0.01-0.3	10-400	—
F	—	—	—	—	—	—	—
Li	—	—	—	—	0.2-10	10-400	—
Ag	0.1-20	0.15-30	0.001-5	—	1-20	10-400	2.6
Sn	—	3-30	0.001-7.5	—	0.2-5	10-400	2.5-32
Fe	0.2-80	1.5-3,000	0.001-4	1-23	1-12	10-400	1%-25%
Sr	0.2-40	0.3-300	—	—	—	10-400	70-570
Na	—	—	0.001-0.05	0.3-11	1-15	10-400	—
K	—	—	—	0.6-1.4	—	10-400	—
Ca	—	—	0.001-0.2	4-21	0.5-5	—	100-9%
Si	—	—	0.001-14	14-41	—	—	15-41
Mg	—	—	0.001-11	0.8-5.5	0.1-1	10-150	0.07%-4.3%
U	—	—	—	—	—	0.5-400	0.5-2400
Th	—	—	—	—	—	50-400	2.5-300

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[a] Index to references in Table 3.

[b] Elements reported as oxides.

Table 3. Index to Emission Spectroscopy References

Column in Table 1	Spectrographic and Spectrometric Emission Sources	References
1	DC Arc in Air	1
2	DC Arc, Li Salt Buffer	2
3	DC Arc, Controlled Atmosphere	3,4,5,6,7
4	DC Arc, Reduced Pressure Argon	8
5	Spark, Porous Cup Rotating Disk	10,11,12,13
6	Spark, Copper and Graphite	15,16,17,18
7	Hollow Cathode	23
8	Flame	24
9	Argon Induction-Coupled Plasma	25

Column in Table 2	Spectrographic and Spectrometric Analysis of Various Materials	References
1	Water, Rotating Disk Method	32a
2	Water, Residue Method	32b, 33a
3	Aluminum, Spark Emission	33a, 33b
4	Coal Ash	45
5	Copper, Globular Arc	36b
6	Minerals and Phosphate Rocks	48
7	Minerals and Powders	52

Table 4. Estimates of Time Required for Several Types of Spectrographic and Spectrometric Analyses.

Type of Analysis	Number[a] of Samples	Number of Elements	Total Time (Hr.)	Time/Element Analysis (Min.)	Comments
Qualitative, Spectrographic	1 15	25 25	1.5 4	2-3 0.5-1	Solids, Powders, or Liquids.
Semiquantitative, Spectrographic	1 12	25 25	4 8	8-12 1-3	Solids or Powders. All samples of like matrices.
Quantitative, Spectrographic	1 1 12	1 25 25	2 5 12	120 10-15 2-4	Solids, Powders. All samples of like matrices.
Quantitative,	1	1	0.25	15	Solids,Powders, or Liquids.
Spectrometric	1 12	25 25	4 6	10 1-3	Direct-Reading Spectrometer with Intensity Ratio Output.
	12	25	0.25	0.05 (3 Sec.)	Direct-Reading Spectrometer with Dedicated Computer and Automatic Printout in Predetermined Format.

(a) For spectrographic analysis, this is the number of exposures that can be conveniently put on a pair of photographic plates in a spectrograph camera.

Optical Emission Spectrometry General References

1B. Morrison, G. H., Ed., "Trace Analysis," Wiley Interscience, New York, 1965.

2B. Cali, J. P., Ed., "Trace Analysis of Semiconductor Materials," Pergamon-Macmillan, New York, 1964.

3B, Harvey, C. E., "Semiquantitative Spectrochemistry," Applied Research Laboratories, Glendale, Calif, 1964.

4B. A.S.T.M., "Methods for Emission Spectrochemical Analysis," Committee E-2 on Emission Spectroscopy, 6th Ed., American Society for Testing and Materials, Philadelphia, Pa., 1971.

5B. Pinta, M., "Detection and Determination of Trace Elements; Absorption Spectrophotometry, Emission Spectroscopy, Polarography," Davey, New York, 1966.

6B. Meinke, W. W., and Scribner, B. F., Eds., "Trace Characterization, Chemical and Physical," Nat. Bur. of Stand., Monogr. 100, U.S. Govt. Printing Office, Washington, D.C., 1967.

Optical Emission Spectrometry Reviews

1R. Dekalb, E. L., Kniseley, R. N., and Fassel, V. A., Optical Emission Spectroscopy as an Analytical Tool, Ann. N. Y. Acad. Sci. 137, 235 (1966).

2R. Barnes, R. M., Emission Spectrometry, Anal. Chem. 44 (5), 122R-150R (1972).

3R. Winefordner, J. D., and Vickers, T. J., Flame Spectrometry, Anal. Chem. 44 (5), 150R-182R (1972).

4R. Margoshes, M., Emission Spectrometry, Anal. Chem. 42 (5), 398R-417R (1970).

5R. Winefordner, J. D., and Vickers, T. J., Flame Spectrometry, Anal. Chem. 42 (5), 206R-231R (1970).

6R. Margoshes, M., and Scribner, B. F., Emission Spectrometry, Anal. Chem. 40 (5), 223R-246R (1968).

7R. Scribner, B. F., and Margoshes, M., Emission Spectrometry, Anal. Chem. 36 (5), 329R-343R (1964).

8R. Norris, J. A., ASTM Symp. Spec. Anal. Trace Elements. American Society for Testing and Materials, Philadelphia, Pa., 1958.

References

1. Ahrens, L. H., and Taylor, S. R., "Spectrochemical Analysis, A Treatise on the d-c Arc Analysis of Geological and Related Materials," 2nd Ed., p. 181, Addison-Wesley, Reading, Mass., 1961.

2. Harvey, C. E., "Semiquantitative Spectrochemistry," Applied Research Laboratories, Glendale, Calif., 1964.

3. Morrison, G. H., Rupp, R. L., and Klecak, G. L., Spectrographic Analysis of High Purity Silicon Carbide, Anal. Chem. 32, 933-935 (1960).

4. ASTM Committee E-2 on Emission Spectroscopy. Methods for Emission Spectrochemical Analysis, 4th Ed., American Society for Testing and Materials, Philadelphia, Pa., 1964.

5. Mittledorf, A. J., The Spex Speaker 7(4), Spex Industries, Inc., Metuchen, N. J., 1962.

6. Morrison, G. H., and Rupp, R. L., In "Silicon Carbide," Edited by J. R. O'Connor and J. Smiltens, p. 227, Pergamon Press, Oxford, 1960.

7. Rupp, R. L., Klecak, G. L., and Morrison, G. H., Spectrographic Analysis of High Purity Nickel, Anal. Chem. 32, 931 (1960).

8. Gordon, W. A., and Chapman, G. B., Quantitative Direct-Current Arc Analysis of Random Compositions of Microgram Residues in Silver Chloride Common Matrix, Spectrochim. Acta 25B, 123-137 (1970).

9. Hambidge, K. M., Use of Static Argon Atmosphere in Emission Spectrochemical Determination of Chromium in Biological Materials, Anal. Chem. 43, 103-107 (1971).

10. Baer, W. K., and Hodge, E. S., The Spectrochemical Analysis of Solutions, A Comparison of Five Techniques. Appl. Spectrosc. 14, 141-146 (1960).

11. Feldman, C., Direct Spectrochemical Analysis of Solutions, Anal. Chem. 21, 1041 (1949).

12. Feldman, J., Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., March 1963.

13a. Wilska, S., Sensitivity of Direct Spectral Analysis of Solutions, Acta Chem. Scand. 5, 890-897 (1951).

13b. Wilska, S., Quantitative Spectral Analysis of Trace Elements in Water, Acta Chem. Scand. 5, 1368-74 (1951).

14. Gerlach, W., and Riedl, E., Spectroanalytical Studies. XIII. The Spectroscopic Test of Purity in the New Primary Radium Standard, Z. Anorg. Chem. 221, 103-108 (1934).

15. Fred, M., Nachtrieb, N. H., and Tomkins, F. S., Spectrochemical Analysis by the Copper Spark Method, J. Opt. Soc. Am. 37, 279-288 (1947).

16. Nachtrieb, N. H., Principles and Practice of Spectrochemical Analysis, pp. 264-285, McGraw-Hill, New York, 1950.

17. Morris, J. M., and Pink, F. X., Symposium on Spectrochemical Analysis for Trace Elements, ASTM Special Technical Publication No. 221, p. 39, American Society for Testing and Materials, Philadelphia, Pa., 1960.

18. Feldman, C., Rare Earths Microanalysis, In Encyclopedia of Spectroscopy, Edited by G. L. Clark, pp. 275-277, Reinhold, New York, 1960.

19. Duffendack, O. S., and Thompson, K. B., Developments in the Quantitative Analysis of Solutions by Spectroscopic Means, Proc. Am. Soc. Testing Materials 36(2), 301-309 (1936).

20. Duffendack, O. S., Analysis of Caustic Liquors for Traces of Impurities, Ind. Eng. Chem., Anal. Ed. 10, 161-164 (1938).

21. Hess, T. M., Owens, J. S., and Reinhardt, L. G., Analysis of Organic Materials for Traces of Metallic Impurities, Ind. Eng. Chem., Anal. Ed. 11, 646-649 (1939).

22. Zhigalovskaya, T. N., Egorov, V. V., Makhon'ko, E. P., Pervunina, R. I., Shilina, A. T., Tr. Inst. Eksp. Meteorol., No. 2, 45-53 (1970); C.A. 74, 115723h (1971).

22a. Pfeilsticker, K., Intermittent Arc with h.f. Excitation, Z. Elektrchem. 43, 717-721 (1937).

22b. Pfeilsticher, K., Experiments with the Self-Igniting Interrupted Arc, Z. Metallkunde 30, 211-14 (1938).

23. Korovin, Y. I., On the Increase of Sensitivity of Determinations by Means of a Hollow Cathode Discharge, Zh. Analit. Khim. 16, 494 (1960).

23a. McNally, J. R., et al., A Hollow Cathode Source Applicable to Spectrographic Analysis for the Halogens and Gases, J. Opt. Soc. Am. 37, 93-98 (1947).

23b. Adams, K. B., and Burns, K., Westinghouse Corp. Research Memo 6-94602-9-M37 (1957).

23c. Thornton, K., The Use of a High Temperature Hollow Cathode Lamp for the Spectrographic Analysis of Steels, High Temperature Alloys, and Related Materials for Trace Elements, Analyst 94, 958-967 (1969).

23d. Ropert, M. E., Use of a Luminescence Discharge Source for Non-Conducting Materials in Spectrographic Analysis, Compt. Rend. 271, 992-994 (1970).

24. Fassel, V. A., and Golightly, D. W., Detection Limits of Elements in the Spectra of Premixed, Oxyacetylene Flames, Anal. Chem. 39, 466-476 (1967).

25. Dickenson, G. W., and Fassel, V. A., Emission Spectrometric Detection of the Elements of the Nanogram per Milliliter Level Using Induction-Coupled Plasma Excitation, Anal. Chem. 41, 1021 (1969).

26. Fassel, V. A., Electrical Flame Spectroscopy, Plenary lecture presented at XVI Colloquium Spectroscopicum Internationale, Heidelberg, Germany, Oct. 1971.

27. Thiers, R. E., Separation, Concentration and Contamination, in "Trace Analysis," Edited by J. H. Yoe and H. J. Koch, Jr., Wiley, New York, 1957.

28. Minczewski, J., Preconcentration in Trace Analysis, in Nat. Bur. Stand., Monogr. 100, U.S. Govt. Printing Office, Washington, D.C., 580 pages (April, 1967).

29. Mizuike, A., Separations and Preconcentrations, Chapter 4 in Trace Analysis, Edited by G. H. Morrison, Wiley-Interscience, New York, 1965.

30. Lighty, P. E., and Currier, E. W., Emission Spectroscopy, Chapter 2 in "Trace Analysis of Semiconductor Materials," Edited by J. P. Cali, Macmillan Co., New York, 1964.

30a. Jackwerth, E., and Graffmann, G., Eine Komplex-Austauchreaktion zur Indirekten Photometrischen und Atomsabsorptions-Spektrometrischen Bestimmung von Spurenelementen, Z. Anal. Chem. 257, 265-268 (1971).

30b. Jackwerth, E., Lohmar, J., and Schwark, G., Anreicherung und Spektrochemische Bestimmung von Spurenelementen in Reinsten Thalliumpräparaten, Z. Anal. Chem. 257, 101-106 (1971).

30c. Jackwerth, E., Döring, E., Lohmar, J., and Schwark, G., Spurenanreicherung Durch Partielles Lösender Matrix, Z. Anal. Chem. 260, 177-184 (1972).

30d. Jackwerth, E., and Kulok, A., Versuche zur Anreicherung von Edelmetallspuren in Reinstquecksilbar Durch Partielles Lösen der Matrix, Z. Anal. Chem. 257, 28-33 (1971).

31a. Kopp, J. F., and Kroner, R. C., A Direct-Reading Spectrochemical Procedure for the Measurement of 19 Minor Elements in Natural Water, Appl. Spectrosc. 19 (5) 155-159 (1965).

31b. Kopp, J. F., and Kroner, R. C., Tracing Water Pollution with an Emission Spectrograph, J. Water Pollution Control Federation 39, 1659-1668 (1967).

31c. Pforr, G., and Aribat, O., Spectrographic Analysis of Solids and Viscous Solutions Using a Plasma Source, Z. Chem. 10, 78-79 (1970).

31d. Sakai, S., Determination of Metallic Ingredients of Waste Water by Rotating Disk Solution Excitation, Bunko Kenkyu 13, 94-102 (1965).

32a. Kopp, J. F., and Kroner, R. C., A Five Year Summary of Trace Metals in Rivers and Lakes of the United States, Oct. 1, 1962; Sept. 30, 1967; U. S. Dept. of Interior, Federal Water Control Administration, Cincinnati, Ohio, 1967.

32b. Haffty, J., Residue Method for Common Minor Elements, U. S. Dept. of the Interior, Geological Survey, Water Supply Paper No. 1540-A, U. S. Govt. Printing Office, Washington, D. C. 1960.

33a. ASTM Committee E-2, Methods for Emission Spectrochemical Analysis, Sixth Ed., American Society for Testing and Materials, Philadelphia, Pa., 1971.

33b. Balfour, B. E., Jukes, D., and Thornton, K., A Spectrochemical Method for the Determination of Trace Impurities in Metallurgical Materials, Appl. Spectrosc. 20, 168-171 (1966).

33c. Killeen, O. P., Spectrographic Detection of Trace Elements in Aluminum Metal, U.S.A.E.C. Report Y-1532, 15 pp (1966).

34a. Tymchuk, P., Russell, D. S., and Berman, S. S., Ottawa Symposium on Spectroscopy, Sept. 1964.

34b. Tymchuk, P., Mykytink, A., and Russel, D. S., Spectrochemical Analysis of Trace Impurities in Copper Using Copper Fluoride as a Carrier-Distillation Agent, Appl. Spectrosc. 22, 268-271 (1968).

35. Elwell, W. T., and Scholes, I. R., "Analysis of Copper and Its Alloys," Pergamon Press, New York, 1967.

36. Dozinel, C. M., "Modern Methods of Analysis of Copper and Its Alloys,"(English translation by G. R. Andraso, Pittsburgh, Pa.), Charles Dozinel, Brussels, 1960.

36a. Tölle, H., Spectrographic Determination of Trace Impurities in Pure Copper Using a Globule Arc in Oxygen, Z. Analyt. Chem. 240, 162-170 (1968).

36b. Publicover, W. E., Spectrochemical Analysis of Oxygen-Free Electrolytically Pure Copper by a Globular Arc Procedure, Anal. Chem. 37, 1680-1684 (1965).

37. Iron and Steel Institute, Spectrographic Analysis of Low Alloy Steels, Special Rpt. No. 47, The British Iron and Steel Research Association, The Iron and Steel Institute, London, 1952.

37a. Atwell, M. G., and Golden, G. S., The Emission Spectrographic Carrier-Distillation Determination of Traces of Lead, Bismuth and Tin in Nickel-Base Alloys, Appl. Spectrosc. 24, 362-364 (1970).

38. Scribner, B. F., and Mullin, H. R., Carrier-Distillation Method for Spectrographic Analysis and its Application to the Analysis of Uranium-Base Materials, NBS J. Res. 37, 379-389 (1946).

38a. Shapiro, L., Developments in Applied Spectroscopy 8, 143-157 (1970).

39. Mittledorf, A. J., Emission Spectrochemical Methods, Chapter 6 in "Trace Analysis," Ed. by G. H. Morrison, Wiley-Interscience, New York, 1967.

40. Collins, A. G., Emission Spectrometric Determination of Barium, Boron, Iron, Manganese, and Strontium in Oilfield Waters Using a Plasma Arc, Appl. Spectr. 21, 16-19 (1967).

41a. Abernethy, R. F., Ergun, S., Friedel, R. A., McCartney, J. T., and Wender, I., Coal and Coke, in Encyclopedia of Industrial Chemical Analysis, V.10, Ed. by F. D. Snell and L. S. Ettre, pp. 209-262, Wiley-Interscience, New York, 1971.

41b. Abernethy, R. F., Peterson, M. J., and Gibson, F. H., Spectrochemical Analysis of Coal Ash for Trace Elements, U. S. Bur. of Mines Report PB 185554, 1969.

42. Sharkey, A. G., Shultz, J. L., and Friedel, R. A., Advances in Coal Spectrometry - Mass Spectrometry, U. S. Bur. Mines Rept. Invest. 6318 (1963).

43. Gibson, F. H., and Ode, W. H., Applications of Rapid Methods for Analyzing Coal Ash and Related Materials, RI 6036, U. S. Bur. Mines, 1962.

44. Suhr, N. H., and Ingamells, C. O., Solution Technique for Analysis of Silicates, Anal. Chem. 38, 730-34 (1966).

45. Karacki, S. S., Coal Ash Analysis with an Argon Plasma Emission Excitation Source, Paper 96, Pittsburgh Conference on Analytical Chemistry and Spectroscopy, Cleveland, March 1972.

46. Ecrement, F., Dosage Elem. Etat Traces Roches Autres Subst. Miner. Natur., Actes Colloq., 173-85 (1968); C. A. 75, 83749y (1971).

47. Govindaraju, K., Dosage Elem. Etat Traces Roches Autres Subst. Miner. Natur., Actes Colloq., 133-44 (1968); C. A. 75, 58276j (1971).

48. Avni, R., and Boukobza, A., Cathode-Region Method for the Direct Spectrochemical Determination of 50 Trace Elements in Rock Phosphate, Appl. Spectrosc. 23, 483-489 (1969).

49. Tennant, W. C., and Sewell, J. R., Direct-Reading Spectrochemical Determination of Trace Elements in Silicates Incorporating Background and Matrix. Correction, J. Quant. Spectrosc. Radiat. Transfer 9, 640-645 (1969).

50. Moal, J. Y., Beguinot, J., Ruel, G., and Vannier, M., The Quantometer for the Direct-Reading Determination of Traces of Elements in Natural Materials, C.N.R.S. Report No. 923, 107-132 (1970).

51. Schoenfeld, I., Spectrochemical Determination of Fluorine in Standard Rocks, Appl. Spectrosc. 24, 359-361 (1970).

52. de Villiers, D. B., van Wamelen, D., and Strasheim, A., Semiquantitative Procedure for the Simultaneous Spectrographic Determination of Thirty Elements in Powder Samples, Appl. Spectrosc. 20, 298-301 (1966).

53. de Montleau, Ph., Spectrographic Analysis with the Tape Machine, Method. Phys. Anal. 6, 162-166 (1970).

CHAPTER 8

VOLTAMMETRY (POLAROGRAPHY)

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1. INTRODUCTION

Voltammetry (polarography) is a well known analytical technique that has considerable potential for environmental analysis. While best known for the determination of trace metals, it can be applied to the determination of some non-metals and to organic compounds as well. In fact, any substance that can be electro-oxidized or reduced in solution is potentially determinable by voltammetry.

Attractive features of voltammetry include high sensitivity, good selectivity, moderate cost of instrumentation, and the ability to determine several constituents in the same solution. Modern instrumentation has improved polarography with respect to sensitivity, selectivity, and ease of operation. Accordingly, it is surprising that the technique has not found more extensive use in environmental analysis.

In this chapter, the voltammetric techniques of analytical importance are described, chemistry pretreatment and matrix effects are discussed, and some of the experience obtained at NBS is mentioned. In addition, applications to environmental pollution found in the literature are reviewed and estimates are given of the types of results which can be expected.

A. Background

With a conventional d.c. pen-recording polarograph and a dropping mercury electrode, solutions containing as little as 1 μg/ml (0.01 millimolar) can be analyzed. Accuracies of 2-5 percent are found, and when reduction potentials are separated by as much as 200 mV, a number of elements can be determined in the same solution.

The sensitivity and resolution of polarographic analysis have been greatly extended by the development of modern instrumentation such as square wave and pulse polarography by Barker and co-workers (1). Of these, pulse polarography has been used most often for analytical purposes, and instruments are commercially available. With this technique short voltage pulses of increasing amplitude are applied to the mercury drop (or a suitable cathode) which is held at the initial potential, and the current is measured near the end of the drop growth. For the differential pulse technique, short voltage pulses of constant amplitude are applied against a linearly increasing background voltage. In both cases the charging current is allowed to decay before the measurement of the faradaic current. Only changes in current are measured; therefore, increased sensitivity is obtained. Concentrations as low as 10 ng/ml can be determined and peaks differing by only 40 mV can be resolved.

Polarographic capabilities have also been improved by the development of cathode ray polarography by Randles, with further improvements by Davis and co-workers (2). With this instrument a linear voltage sweep is applied, in either the anodic or cathodic direction, during the last two seconds of the life of a mercury drop which is mechanically detached every seven seconds. The peak resulting from the electro-oxidation (or reduction) of the species in question, and which is proportional to its concentration, is displayed and measured on a cathode ray tube or a fast recorder. Sensitivities of 10 to 50 ng/ml can be obtained and peaks differing by less than 100 mV can be resolved.

By use of dual cells, differential operation may be obtained with this polarograph. Electrodes are matched by cutting a capillary into two pieces of equal length and using the cut faces as the dropping orifices. The drop masses are equalized by adjustment of the heads of the two mercury columns immersed in portions of the same solution to give identical reduction peak heights for each cell. For subtractive polarography, the second cell contains the blank, and its signal is electrically subtracted from that of the first cell containing the sample, giving much better defined peaks and higher sensitivity. In the same way, interfering peaks may be minimized by putting a similar amount of the interfering ion or ions in the second cell.

The best polarographic precision obtainable, so far, can be achieved by using the second cell in the comparative mode of operation; that is, placing in it a very accurately known standard, similar in concentration to the sample which is in the other cell. The very small difference between the two is then amplified and measured. By this technique, standard deviations as low as 2 to 5 parts in 10,000 have been obtained (3, 4). This makes possible highly accurate determination of macro constituents on micro amounts of sample.

The highest polarographic sensitivity, ranging from 1 ng/ml to 1 pg/ml can be obtained by anodic stripping utilizing any of the newer instrumentation presently available. This technique involves plating onto a cathodic electrode for a fixed length of time at an appropriate potential, then applying a voltage scan in the anodic direction, measuring the increased peak current resulting from the oxidation of the ion or ions in question which were accumulated on the electrode. A variety of types of electrodes may be used - including hanging mercury drop (either extruded or plated onto platinum or gold), thin film and solid electrodes, such as composite mercury-graphite, glassy carbon, etc. Cathodic stripping, which is the reverse of the procedure described above, can be used for determination of anions.

2. APPLICATIONS TO ENVIRONMENTAL ANALYSIS

Voltammetric analysis requires that the substances of interest be dissolved and contained in an electrolyte of favorable composition. Proper selection of this supporting electrolyte can also minimize interferences in the case of complex mixtures.

For simplification, the 12 matrices of interest have been combined into three separate groups. In some respects this is an oversimplication, as any one of the matrices may require some individual consideration. These groupings have been based, not necessarily on the similarities of the matrix, but rather on the complexity of sample dissolution and of other chemical pretreatments which may be necessary before the instrumental measurement. Fly ash, coal, oil, organometallics, incinerator particulates, and minerals are grouped together, because in most cases the matrix consists of carbon, organic matter, and/or silica, all of which can be readily eliminated by wet ashing with nitric, perchloric and/or hydrofluoric acids, leaving the ion of interest in a soluble form. The minerals in a few cases may consist, instead, largely of a heavy metal matrix rather than silica, and in such cases should be classified with ores, metals, and alloys. For the first group of matrices, supporting electrolytes may be chosen so that few direct interferences will exist for most of the ions of interest. In some cases better accuracies may be obtained because of increased resolution after a simple separation such as solvent extraction.

For ores, metals, and alloys, supporting electrolytes may be chosen for the specific problem at hand so that few direct interferences exist; however, the matrix materials (such as iron, lead, or zinc, etc.) may have a reduction potential in the vicinity of the ion in question, and which in excessive concentrations could decrease the resolution so that separation may be advisable. Ferric iron is reduced fairly close to zero volts, in many supporting electrolytes; hence if it is the major constituent, it may swamp out trace amounts of other ions reduced near zero volts. It may be extracted by a variety of means such as chloroform - cupferron, isobutyl acetate, or methyl isobutyl ketone. A much simpler solution, however, is to treat it with a reducing agent such as ascorbic acid or hydroxylamine hydrochloride converting it to ferrous iron which is reduced at a much more negative potential.

Lead may be eliminated in most cases by the addition of sulfate. Subsequent filtration is not necessary as the precipitated lead sulfate may be allowed to remain in the solution. Iron, in most cases, cannot be removed as a matrix interferant in a similar manner by precipitation with base, because the iron hydroxide precipitate is a colloidal, gelatinous one which could occlude trace metals of interest.

The zinc matrix causes no interference in most cases, as its reduction potential is more negative than most of the ions of interest.

For slurry streams, feeds to/and from flotation processes, sediments in flotation processes, effluents and water in general, water, which may comprise the bulk of the matrix, can be removed simply by evaporation. The remainder of residual material will fall under the classification of one of the first two groups and it can be treated in a similar manner. The presence of calcium, or other alkaline earths or alkalis present no problems, as they are all reduced at a sufficiently negative potential to cause no interference with the ions of interest in this study.

Cadmium in air has been determined by a number of workers after collection on cotton or glass wool plugs, filter paper, electrostatic precipitators or impingers. Silverman (5) determined cadmium in dust and fumes using several of these collection techniques. After dissolution of the collected sample and oxidation of the organic material with nitric acid and hydrogen peroxide and evaporation to dryness, cadmium was measured polarographically at -0.63V in a supporting electrolyte containing ammonium hydroxide and potassium chloride. Other workers (6) have used an ammonium chloride - ammonium hydroxide or a 30 percent ammonium acetate supporting electrolyte, and have also determined copper and zinc at the same time.

Landry (7) determined lead and zinc in the atmosphere using cadmium and manganese as internal standards, in an ammonium chloride-ammonium hydroxide supporting electrolyte. Earlier workers (8) determined lead in 0.1N KCl by addition of a known amount of either zinc or cadmium as an internal standard. This method requires that zinc or cadmium not be present in the sample. Kito (9) determined lead in 50-1000 ml samples of air using a supporting electrolyte of potassium nitrate, glycine and nitric acid at a pH of 3.

Tetraethyl lead in air was determined by Khlopin (10) after absorption of about 0.5 cubic meter of air in castor oil containing a saturated solution of iodine in methyl alcohol. The mixture was digested with nitric acid and evaporated to dryness. The residue was dissolved in dilute hydrochloric acid and measured in a 30 percent calcium chloride solution. Khlopin (11) used the same supporting electrolyte for the determination of zinc, lead, copper, cadmium, manganese, and bismuth in air. He reports that all six elements may be determined simultaneously.

Urone and coworkers (12) have described a micromethod for the determination of chromium in dusts and mists. After suitable pretreatment, chromium was oxidized with hydrogen peroxide and measured in 1N sodium hydroxide. The limit of sensitivity was about 0.05 μg/ml in the final solution and the error was ± 4 percent.

A method has been described for the determination of manganese, chromium, and iron in air in a triethanolamine-sodium hydroxide supporting electrolyte (13). Pines (14) used a similar supporting electrolyte and determined amounts down to 20 μg of manganese in air with coefficients of variation of 8.5 percent. For 500-800 μg of manganese, the coefficient of variation was 2.5 percent.

Babina (15) determined titanium in air after absorption in 0.5 M sulfuric acid or collection on a PVC filter. Potassium oxalate was used as a supporting electrolyte and the pH of the solution was adjusted to 3 - 3.5 with potassium hydroxide. Errors of ± 6 percent were obtained, and more than 50 μg/ml of iron and 1 μg/ml of vanadium interfered.

Arsine in gas mixtures has been determined by utilization of its anodic wave in a supporting electrolyte of ethanol and ammonium nitrate (16). Phosphine and stibine give waves at the same potential, hence would interfere.

Particulates collected in laboratory air, suburban air, rural air, and industrial air have been analyzed at the National Bureau of Standards by cathode ray polarography for iron, copper, lead, and cadmium; all four elements could be measured concurrently without separations, after wet ashing (17,18). Bulk particulate matter under study as a possible standard reference material was readily analyzed for copper, lead, cadmium, and zinc in the same solution (19).

Metal organics including quinolates and cyclohexanebutyrates have been readily analyzed for copper, nickel, manganese, iron, zinc, lead, or cadmium, directly after dry or wet ashing of the sample (17,20). Most of these determinations were at the major constituent level, hence the determinations required only a few mg. of sample. Cadmium at the 25 percent level was determined directly in cadmium cyclohexanebutyrate after dry ashing. Standard deviations of 0.15 percent were obtained using the double cell comparative method (18).

Iron, copper, nickel, lead and aluminum have been determined in lubricating oils at the 1-, 50-, and 500- ppm level respectively, after dry ashing. These mixtures had been prepared as possible standards for monitoring engine wear and predicting engine failure (21).

Glass, rocks, and soils have been readily analyzed by polarography. Iron, titanium and nickel have been determined at the 1-, 50-, and 500-ppm levels in a series of doped glass standard reference materials (22), with standard deviations of about 1 to 2 percent. The results agreed very well with those found by several other techniques (23).

Iron, titanium, and nickel have been determined in lunar rocks and fine soil from the Apollo 14, 15 and 16 flights. All three elements can be determined in a single 5-mg sample. The iron values for the different samples ranged from 3.5 to 15 percent; titanium, from 0.3 to 1.3 percent; and nickel, from 100 to 400 ppm (24).

Polarography has been useful in the analysis and certification of several of the NBS botanical Standard Reference Materials which present many of the same analytical problems as organics and particulates. Iron, aluminum, lead, cadmium, bismuth and nickel are all readily determined in amounts ranging from 0.1 to 350 ppm (25).

A considerable portion of the polarographic work at NBS has been concerned with metal and alloy analysis; hence, the usefulness of polarography in this application is amply demonstrated (4, 17-21). It has been used for rapid identification and analysis of metals and alloys in very small amounts of sample, and it should be applicable to the analysis of particulates from slurry streams, sediments, and fly ash. Identification of corrosion products is another one of NBS experiences that has applications of environmental interest.

Complete compositional analyses have been made on samples as small as 90 μg in the case of thin films composed of antimony-bismuth, lead-tin-tellurium, nickel-chromium-aluminum-copper, and lead-selenium (17, 18, 20, 21).

Various types of effluents and water systems have proved to be amenable to polarographic analysis. Periodic analyses have been made of copper and zinc in the local water supply to evaluate its suitability for use in a proposed National Aquarium. Water samples (100-500 ml) were filtered, the organic material destroyed by acid treatment, and the samples evaporated to dryness. The residues were dissolved in dilute hydrochloric acid and the solutions made ammoniacal. Copper and zinc were determined concurrently on the cathode-ray polarograph from peaks appearing at -0.4 V and -1.2 V, respectively. By use of the sample sizes indicated, the method was applicable down to at least 5 ppb of copper and zinc.

Samples of water from the NBS reactor have been routinely monitored for several elements including copper, cadmium, lead, iron, and aluminum directly, with no separations, in amounts ranging from 0.6 to 200 ppb.

3. CONCLUSIONS

The examples discussed here demonstrate the applicability of polarography to trace element determination in materials similar to the matrices under consideration. Additional applications found in the literature are given in the Bibliography. Tables 1, 2, and 3 give a summary of sensitivities, accuracies and costs that can be expected for typical samples. In many cases the sensitivities achieved could be significantly greater and the cost of analysis could be considerably less than those indicated in the tables, with the expenditure of a little effort to optimize methodology. The sensitivities indicated in the tables are in general poorer than those given in instrumentation discussions for pure solutions, because a realistic evaluation has been made on the basis of problems which can occur with real samples. One of the main limits to the sensitivity achievable on real samples is the magnitude of the blank (both from reagents and from the environment). If the blank can be kept to a low level, then higher sensitivity can be achieved.

The prices for commercial voltammetric instrumentation range from about $3,000 to $16,000. No additional equipment should be required other than that present in an ordinary chemical analytical laboratory.

A technician, well-trained in analytical manipulations, should be capable of performing most of the analyses, provided a detailed procedure is available. A competent electroanalytical chemist should be available for consultation.

Table 1. Analysis of Fly Ash, Coal, Oil, Organometallics, Incinerator Particulates, and Minerals by Polarography

Element(a)	Accuracy(b) (%)	Time to(c) Prepare Sample (hr)	Detection Limit (ppm)	Sample(d) Size (g)	Cost(c) Per Analysis ($)	Comments(e)
Cd	0.1-10	0.5	10 ppb	1	3	In interferes(f)
As	2-15	1	0.5	1	6	(f)
V	2-15	2	0.5	1	12	(f)
Mn	2-15	2	0.1	1	12	(f)
Ni	2-15	1	0.1	1	6	(f)
Sb	2-15	1	0.1	1	6	(f)
Cr	0.2-15	1	0.1	1	6	Pb,Zn interfere(f)
Zn	0.2-15	1	0.1	1	6	(f)
Cu	0.2-15	1	0.1	1	6	(f)
Pb	0.2-15	1	0.1	1	6	Tl interferes(f)
Se	2-15	2	1	1	12	(f)
Sn	0.5-15	2	0.5	1	12	(f)
Fe	0.2-15	1	0.1	1	6	(f)
U	0.2-15	2	0.2	1	12	(f)

(a) Polarography not often used for: Hg, Be, B, F, Li, Ag, Sr, Na, K, Ca, Si, Mg, Th.

(b) Accuracy range: standard deviation (%) at macro constituent level to standard deviation at detection limit, by differential polarography.

(c) Time & costs based on sets of six samples, single-element determinations. Costs are considerably less for multi-element determinations in the same sample.

(d) Sample size requirement for elemental determination at stated detection limits. Larger samples give lower detection limits; smaller samples required for more abundant elements.

(e) See text for equipment and manpower requirements.

(f) Interfering elements can be separated.

Table 2. Analysis of Ores, Metals, and Alloys by Polarography

Element(a)	Accuracy(b) (%)	Time to(c) Prepare Sample (hr)	Detection Limit (ppm)	Sample(d) Size (g)	Cost(c) Per Analysis ($)	Comments(e)
Cd	0.1-10	1	50 ppb	1	6	In interferes(f)
As	2-15	2	1	1	12	(f)
V	2-15	2	1	1	12	(f)
Mn	2-15	2	1	1	12	(f)
Ni	2-15	1	0.5	1	6	(f)
Sb	2-15	1	1	1	12	(f)
Cr	2-15	1	1	1	12	Pb,Cu interfere(f)
Zn	0.2-15	1	1	1	12	(f)
Cu	0.2-15	1	0.5	1	12	(f)
Pb	0.2-15	1	0.2	1	6	(f)
Se	2-15	2	5	1	12	(f)
Sn	2-15	2	1	1	12	(f)
Fe	0.2-15	1	1	1	12	(f)
U	0.2-15	2	1	1	12	(f)

(a) Polarography not often used for: Hg, Be, B, F, Li, Ag, Sr, Na, K, Ca, Si, Mg, Th.

(b) Accuracy range: standard deviation (%) at macro constituent level to standard deviation at detection limit, by differential polarography.

(c) Time & costs based on sets of six samples, single-element determinations. Costs are considerably less for multi-element determinations in the same sample.

(d) Sample size requirement for elemental determination at stated detection limits. Larger samples give lower detection limits; smaller samples required for more abundant elements.

(e) See text for equipment and manpower requirements.

(f) Interfering elements can be separated.

Table 3. Analysis of Slurry Streams, Sediments, Process Feeds, and Water by Polarography

Element[a]	Accuracy[b] (%)	Time to[c] Prepare Sample (hr)	Detection Limit (ppm)	Sample[d] Size (g)	Cost[c] Per Analysis ($)	Comments[e]
Cd	0.2-10	0.5	10 ppb	1	6	In interferes[f]
As	2-15	1	0.5	1	6	(f)
V	2-15	2	0.5	1	12	(f)
Mn	2-15	2	0.1	1	12	(f)
Ni	2-15	1	0.1	1	6	(f)
Sb	2-15	1	0.1	1	6	(f)
Cr	0.2-15	1	0.1	1	6	(f)
Zn	0.2-15	0.5	0.1	1	3	(f)
Cu	0.2-15	0.5	0.1	1	3	(f)
Pb	0.2-15	0.5	0.1	1	3	Tl interferes[f]
Se	2-15	2	0.5	1	12	(f)
Sn	0.5-15	2	0.5	1	12	(f)
Fe	0.2-15	1	0.1	1	6	(f)
U	0.2-15	2	0.1	1	12	(f)

(a) Polarography not often used for: Hg, Be, B, F, Li, Ag, Sr, Na, K, Ca, Si, Mg, Th.

(b) Accuracy range: standard deviation (%) at macro constituent level to standard deviation at detection limit, by differential polarography.

(c) Time & costs based on sets of six samples, single-element determinations. Costs are considerably less for multi-element determinations in the same sample.

(d) Sample size requirement for elemental determination at stated detection limits. Larger samples give lower detection limits; smaller samples required for more abundant elements.

(e) See text for equipment and manpower requirements.

(f) Interfering elements can be separated.

Table 4. Element Index to References
Fly Ash, Coal, Oil, Organometallics, Incinerator Particulates and Minerals by Polarography

Element Determined	References
Mercury	
Beryllium	
Cadmium	2,3,6,7,11,12,13,16,25,29,30,32,42,164
Arsenic	2,17
Vanadium	40
Manganese	2,17,25,30,32,34,35,36,43
Nickel	13,13a,18,164
Antimony	3,17
Chromium	15,32,36,46b,46c
Zinc	2,3,11-14,17,25,29,30,31,32,41-44,46c,164
Copper	2,3,8-14,16,25,30,42,46b,46c,164
Lead	2,3,12,13a,16,17,20-32,42,46b,164
Selenium	
Boron	
Fluorine	
Lithium	33
Silver	
Tin	37,46b
Iron	2,13a,17,18,36,46b,164
Strontium	
Sodium	1
Potassium	1
Calcium	
Silicon	
Magnesium	19
Uranium	37a,38
Thorium	
Reviews	45,46,46a

Table 5. Element Index to References
Ores, Metals, and Alloys by Polarography

Element Determined	References
Mercury	
Beryllium	
Cadmium	54,57,58,62,68,69,78,85,86,92,93,96-99,116,117, 121-123,126
Arsenic	47,52,71,81,83,95,100
Vanadium	
Manganese	51,53,100
Nickel	50,53,60,70,78,99,103,113,117
Antimony	47,53,69,70,78,82,90,94,99,119
Chromium	70,75
Zinc	51,55,62,66,75,77,78,80,86,92,98-100,103,104 110-113,116-118
Copper	48,55,59,62,68,69,70,72-75,78,84,86,91,94,99,100, 103,113-117,119,121,123,124
Lead	48,53,56-59,62,67,69,70,73,74,76-78,84,86,87,92-94, 99,100,103-105,114-116,119-121,125-127
Selenium	61,62,106
Boron	
Fluorine	
Lithium	
Silver	88
Tin	47,69,70,78,79,89,90,93,103,107,108,126,128,129
Iron	53,69,91,99,104,117,121,124
Strontium	
Sodium	
Potassium	
Calcium	
Silicon	
Magnesium	
Uranium	109
Thorium	
Thallium	49,65,85,122,126,127
Tellurium	52,62,63,64,69,70,106
Reviews	101,102,131,132

Table 6. Element Index to References
Slurry Streams, Sediments, Process Feeds, and Water by Polarography

Element Determined	References
Mercury	
Beryllium	
Cadmium	147,151,154,155,162,163,165,167,181-184
Arsenic	142-145
Vanadium	162,178
Manganese	147,153,169
Nickel	154-156,162,167,169,178
Antimony	141
Chromium	178
Zinc	140,147,151,153-155,158.162,165,167,168 179-185
Copper	139,147-149,151-158,162,166,167,182-184
Lead	139,147,151,155,157,159,160,163,165-168 182-184
Selenium	171
Boron	
Fluorine	
Lithium	137
Silver	
Tin	140,165
Iron	139,147,162,185
Strontium	
Sodium	135,136,137
Potassium	135,136
Calcium	135,136,138,178
Silicon	
Magnesium	135,136,178
Uranium	172-177
Thorium	
Bismuth	146
Reviews	170,186,187

References

(1) Barker, G. C., and Gardner, A. W., Pulse Polarography, Z. Anal. Chem., 173, 79 (1960).

(2) Davis, H. M., and Seaborn, J. E., "A differential cathode ray polarograph," in Advances in Polarography, (I. S. Longmuir, ed.) Vol. I, Pergamon, London, 1960, p. 239.

(3) Shalgosky, H. I., and Watling, J., High precision comparative polarography, Anal. Chim. Acta, 26, 66 (1962).

(4) Maienthal, E. J., and Taylor, J. K., Improvement of polarographic precision by a comparative technique, Mikrochim. Acta, 1967, 939.

(5) Silverman, L., Simple polarographic procedures for cadmium dust and fumes in air, Chemist Analyst, 35, 53-5 (1946).

(6) Bykhovskaya, M. S., and Poletaev, M. I., Polarographic method in hygienic investigations, Gigiena i Sanit., 1952, 47-50.

(7) Landry, A. S., Simultaneous determination of lead and zinc in atmospheric samples. A polarographic method utilizing a double internal standard, J. Ind. Hyg. Toxicol., 29, 168-74 (1947).

(8) Cantarow, A., and Trumper, M., "Lead Poisoning," 264, Williams and Wilkins Co. (1944).

(9) Kito, T., Measurement of lead in air dust by polarography, Igaku Kenkyu , 23, 1289-1308 (1952).

(10) Khlopin, N. Ya, and Litvinova, N. S., Separation of tetraethyl lead from air and its polarographic determination, Zavod. Lab., 15, 677-8 (1949).

(11) Khlopin, N. Ya., Air-borne lead, copper, cadmium, zinc, manganese, and bismuth, Zavod. Lab., 14, 156 (1948).

(12) Urone, P. F., Druschel, M. L., and Anders, H. K., Polarographic microdetermination of chromium in dusts and mists, Anal. Chem., 22, 472-6 (1950).

(13) Bykhovskaya, M. S., and Orlova, I. A., Determination of manganese, chromium and iron in air by a polarographic method, Zavod. Lab., 27, 540 (1961).

(14) Pines, I., Determination of manganese in industrial atmospheres, Chemia Analit., 12, 1013-1030 (1967).

(15) Babina, M. D., Polarographic determination of titanium in air, Zavod. Lab., 28, 549 (1962).

(16) Vasak, V., Polarographic determination of arsine in gas mixtures, Coll. Czech. Chem. Commun., 24, 3500-3504 (1959).

(17) Maienthal, E. J., Polarographic analysis in NBS Tech. Note 505, Taylor, J. K., ed., p. 36 (1969).

(18) Maienthal, E. J., Polarographic analysis in NBS Tech. Note 545, Taylor, J. K., ed., p. 53 (1970).

(19) Maienthal, E. J., Polarographic analysis in NBS Tech. Note 583, Durst, R. A., ed., p. 39 (1973).

(20) Maienthal, E. J., Polarographic analysis in NBS Tech. Note 455, Taylor, J. K., ed., p. 23 (1968).

(21) Maienthal, E. J., Polarographic analysis in NBS Tech. Note 403, Taylor, J. K., ed., p. 34 (1966).

(22) Provisional Certificate for Trace Elements in a Glass Matrix (SRMs 610-619), Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C., 20234 (8/5/70; revised 8/8/72).

(23) Maienthal, E. J., Determination of trace elements in silicate matrices by differential cathode ray polarography, Anal. Chem., 45, 644 (1973).

(24) Maienthal, E. J., The determination of iron, titanium and nickel in Apollo 14 samples by cathode ray polarography, J. Res. NBS, 76A, 517 (1972).

(25) Maienthal, E. J., Analysis of botanical standard reference materials by cathode ray polarography, J. Assoc. Official Anal. Chemists, 55, 1109 (1972).

Bibliography

A. Fly Ash, Coal, Oil, Organometallics, Incinerator Particulates and Minerals

1. Skobets, V. D., Abarbarchuk, I. L., and Skobets, E. M., Determination of total exchange alkalis in soil by differential polarography, Nauch. Dokl. Vyssh. Shkoly. Biol. Nauk., 1962, 189-193.

2. Maienthal, E. J., Paulson, R. A., and Taylor, J. K., "Applications of polarography to the analysis of air pollutants," (As, Bi, Cd, Cu, Fe, Pb, Mn, Zn, Ge, Tl). Talk presented at the 157th National Meeting, American Chemical Society, Minneapolis, Minnesota, April (1969).

3. Florence, T. M., Determination of trace metals in marine samples by anodic stripping voltammetry, (Bi, Sb, Cu, Pb, In, Cd, Tl, Zn), in press.

4. Rüssel, H., Polarographic determination of small amounts of bismuth in rocks and ores, Z. Anal. Chem., 189, 256-261 (1962).

5. Weiss, D., Oscillographic determination of bismuth and chloride ion, J. Electroanal. Chem., 5, 62-67 (1963).

6. Maienthal, E. J., Cadmium in cadmium cyclohexanebutyrate, Polarographic Analysis, NBS Tech. Note 545, Taylor, J. K., ed., (1970).

7. Silverman, L., Simple polarographic procedure for cadmium dust and fumes in air, Chemist Analyst, 35, 53-55 (1946).

8. Korshunov, A. and Sazanova, L. N., Polarographic determination of copper in peat ash, Zavod. Lab., 14, 238 (1948).

9. Malyuga, D. P., Determination of copper in rocks, soils, and organisms by a polarographic method, Trav. Lab. Biogeochim. Acad. Sci. U.R.S.S., 7, 86-97 (1944).

10. Maienthal, E. J., Analysis of bis (1-phenyl-1, 3-butanediono copper (II), Polarographic Analysis, 17, NBS Tech. Note 505, Taylor, J. K., ed., (1969).

11. Bychovskaja, M. S., and Poletajev, M. I., (Cu, Cd, and Zn in air), Gigiena i Sanit., 12, 47 (1952).

12. Maienthal, E. J., Copper, lead, cadmium and zinc in particulates, Polarographic Analysis, NBS Tech. Note 583, Durst, R. A., ed., in press.

13. Smythe, L. E., and Gatehouse, B. M., Polarographic determination of traces of copper, nickel, cobalt, zinc and cadmium in rocks, using rubeanic acid and 1-nitroso-2-naphthol, Anal. Chem., 27, 901-903 (1955).

13a. Maienthal, E. J., Cu, Ni, Pb, Fe, and Al in lubricating oils, Polarographic Analysis, NBS Tech. Note 403, Taylor, J. K., ed., (1966).

14. Jones, G. B., The polarographic determination of copper and zinc in plants and soils, Anal. Chim. Acta, 7, 578-84 (1952).

15. Urone, P. F., Druschel, M. L., and Anders, H., Polarographic microdetermination of chromium in dusts and mists, Anal. Chem., 22, 472-476 (1950).

16. Sinyakova, S. I., Polarographic determination of indium, cadmium, lead, and copper in sphalerites and other minerals, Zhur. Anal. Khim., 1, 241-249 (1946).

17. Khalafalla, S. E., and Farah, M. Y., Polarographic analysis of complex calamines. Determinations of iron, lead, zinc, manganese, arsenic and antimony, J. Chim. Phys., 54, 251-257 (1957).

18. Maienthal, E. J., The determination of Fe, Ti, and Ni in Apollo 14 samples by cathode ray polarography, J. Res. NBS, 76A, 517-520 (1972).

19. Ferenczy, Z., Almasy, A., and Szadeczky-Kardoss, G., Polarographic determination of magnesium, Acta Chim. Acad. Sci Hung., 9, 179-184 (1956).

20. Nangniot, P., Determination of Pb in H_2O, petrol and biological materials by differential oscillopolarography, Chim. Analyt., 47, 592 (1965).

21. Cantarow, A., Trumper, M., "Lead Poisoning," Williams and Wilkins Co., 264 (1944).

22. Khlopin, N. Ya., and Litvinova, N. S., Separation of tetraethyl lead from air and its polarographic determination, Zavod. Lab., 15, 677-678 (1949).

23. Borup, R., and Levin, H., Polarographic determination of tetraethyl lead in gasoline, Am. Soc. Testing Materials, Proc., 47, 1010-16 (1947).

24. Maienthal, E. J., Lead in industrial air and laboratory air, "Polarographic analysis," NBS Tech. Note 583, in press, NBS Tech. Note 545, 53-5 (1970).

25. Khlopin, N. Ya., Polarographic determination of metal aerosols (Bi, Pb, Cu, Cd, Zn, Mn), Zavod. Lab., 14, 156-8 (1948).

26. Bykhovskaya, M. S., and Poletaev, M. I., Polarographic method in hygienic investigations, Gigiena i Sanit., 12, 47-50 (1952).

27. Kito, T., Measurement of lead in air dust by polarography, Igaku Kenkyu , 23, 1289-1308 (1953).

28. Zhirova, V. V., Oscillopolarographic determination of the lead content of standard G-1 and W-1 rock samples and of rocks with low lead content, Geokhimiya, 1962, 542-4.

29. Feicht, F. L., Schrenk, H. H., and Brown, C. E., Determination with the dropping-mercury-electrode-procedure of lead, cadmium and zinc in samples collected in industrial hygiene studies, U. S. Bureau Mines, Rept. Investigations, 3639, 20 pp. (1942).

30. Khlopin, N. Ya., Air-borne lead, copper, cadmium, zinc, manganese, and bismuth, Zavodskaya Lab., 14, 156 (1948); Zhur. Anal. Khim., 12, 55 (1947).

31. Maienthal, E. J., Analysis of Pb and Zn cyclohexanebutyrates, Polarographic Analysis, NBS Tech. Note 455, 19, (1968).

32. Levine, J., Polarographic determination of toxic metal fumes in air, (Pb, Zn, Cd, Cr, Mn), J. Ind. Hyg. Toxicol., 27, 171-177 (1945).

33. Voigt, A., Polarographic determination of lithium in silicates, Z. Anal. Chem., 133, 44-6 (1951).

34. Pines, I., Determination of manganese in industrial atmospheres, Chemia Analit., 12, 1013-1030, (1967).

35. Kogan, I. B., and Makhover, S. L., Polarographic determination of manganese in air, Gigiena i Sanit., 1954 52-3.

36. Bykhovskaya, M. S., and Orlova, I. A., Determination of manganese, chromium and iron in air by a polarographic method, Zavod. Lab., 27, 540-2 (1961).

37. Hoedt, W., Polarographic determination of tin and bismuth in rocks, Z. Angew. Geol., 8, 529-31 (1962).

38. Ballenger, H. F. (Uranium in Air), U. S. Govt. Pub. AECD-20, 65 (1944).

39. Matres, R. W., and Burastero, J. J., Polarographic determination of uranium in monazite sands, Analyst, 96, 579-83 (1971).

40. Sulcek, Z., Rapid analytical methods for metals and minerals. III Polarographic determination of vanadium in minerals, Chem. Listy, 51, 1453-6 (1957).

41. Takazawa, F., and Sherman, G. D., Polarographic determination of zinc in soil, J. Assoc. Official Agr. Chem., 30, 182-6 (1947).

42. Cohen, E., Determination of micro amounts of heavy metals in air by anodic-stripping voltammetry, (Zn, Cu, Pb, Cd), Bull. Soc. Chim. Fr., 1972, 416-9.

43. Jones, G. B., The polarographic determination of zinc and manganese in plant and animal tissues and soils, Anal. Chim. Acta, 11, 88-97 (1954).

44. Kogan, I. B., Polarographic determination of zinc oxide in the atmosphere, Zavod. Lab., 16, 932-4 (1950).

45. Pignataro, N., Polarographic analysis in mineralogy, Rend. Soc. Mineral. Ital., 71, 71-96 (1947).

46. Sinyakova, S. T., Polarographic analysis of mineral raw materials, Trudy Komissii Anal. Khim., Otdel. Khim Nauk, Akad. Nauk S.S.S.R., 2, 133-56 (1949).

46a. West, P. W., and Hale, C. H., Application of polarography in the petroleum industry, Petroleum Refiner, 29, 109-11 (1950).

46b. Korshunov, I. A., and Shchennikova, M. K., Polarographic determination of metals in used lubricating oils (Cr, Fe, Sn, Pb, Cu), Zavod. Lab., 13, 682-6 (1947).

46c. Korshunov, I. A., Sazanova, L. N., and Protsenko, R. V., Use of polarographic method in analysis of ash components of coal (Cu, Zn, Cr), Zavod. Lab., 13, 301-3 (1947).

B. Metals, Alloys, and Ores

Cadmium

47. Temmerman, E., and Verbeek, F., The determination of traces of Sb, Sn, and As in Cd by pulse polarography, Anal. Chim. Acta, 43, 263-72 (1968).

48. Temmerman, E., and Verbeek, F., Determination of traces of Bi, Cu, and Pb in Cd by pulse polarography, J. Electroanal. Chem., 12, 158-165 (1966).

49. Temmerman, E., and Verbeek, F., The determination of traces of Tl in Cd by pulse polarography, J. Electroanal. Chem., 19, 423-9 (1968).

Cobalt

50. Lagrou, A., and Verbeek, F., The determination of traces of nickel in Co by pulse polarography, J. Electroanal. Chem., 19, 125-9 (1968).

51. Lagrou, A., and Verbeek, F., The determination of traces of Zn and Mn in Co by pulse polarography,, J. Electroanal. Chem., 19, 413-21 (1968).

Copper, Copper Base, Brass and Bronze

52. Cathro, K. J., Polarographic determination of arsenic and tellurium in copper, Aust. J. Appl. Sci., 9, 255-264 (1958).

53. Eve, A. J., and Verdier, E. T., Polarographic determination of traces of bismuth, iron, lead, antimony, nickel, cobalt and manganese in refined copper, Anal. Chem., 28, 537-8 (1956).

54. Fleury, M., and Capelle, R., Polarographic determination of cadmium in bronze, Chim. Anal., 45, 193-8 (1963).

55. Maienthal, E. J., and Taylor, J. K., Improvement of polarographic precision (Cu and Zn in Brass and Bronze), Microchim. Acta, 1967, 939.

56. Milner, G. W. C., Polarographic determination of lead in brasses and bronzes, Analyst, 70, 250-3 (1945).

57. Spalenka, M., Polarographic determination of lead and cadmium in copper and its alloys, Metallwirtschaft, 23, 341-3 (1944).

58. Fleury, M., and Capelle, R., Polarographic determination of lead and cadmium in copper - aluminum alloys, Chim. Anal., 45, 117-123 (1963).

59. Capaccioli, T., Sbrolli, W., and Vercellone, A., Rapid polarographic analysis of lead and copper in commercial brass, Ann. Chim., Roma, 49, 1125-1142 (1959).

60. Milner, G. W. C., Polarographic determination of nickel in copper-base alloys, Analyst, 70, 468-74 (1945).

61. Zopatti, L. P., and Cornwell, J. C., Determination of Se in Cu by cathode ray polarography, in press.

62. Ripen, R., and Pop, G., Ascorbic acid in polarographic analysis, (Se, Fe, Pb, Zn, Cd, in Cu and anodic mud during Cu electrolysis), Rev. Chim., 14, 411-12 (1963).

63. Maienthal, E. J., and Taylor, J. K., Determination of tellurium by cathode-ray polarography (in brass and cast iron), Anal. Chem., 37, 1516 (1965).

64. Bykov, I. E., and Gorshkova, L. S., Polarographic determination of tellurium in copper alloys, Zavod. Lab., 25, 674-76 (1959).

65. Gertseva, N. S., Polarographic determination of Tl in presence of Cu without their preliminary separation, Teoriya i Praktika Polyarograf. Analiza, Akad. Nauk Moldavsk, SSR, Materialy Pervogo Vses. Soveshch., 1962, 222-9.

66. Milner, G. W. C., Applications of the polarograph to metallurgical analysis. II. Polarographic methods for the determination of zinc in copper-base alloys, Metallurgia, 35, 265-7 (1947).

67. Toropova, V. F., Polarographic determination of lead in lead bronzes, J. Applied Chem., 18, 177-80 (1945).

Ga Arsenide

68. Jennings, V. J., Determination of some trace impurities in gallium arsenide by square-wave polarography, (Bi, Cu, In, Cd), Analyst, 87, 548-557 (1962).

Steels, Alloys

69. Maienthal, E. J., "Determination of trace elements in steels, alloys, and other metals by cathode ray polarography" (Al, Pb, Bi, Te, Sb, Sn, Ti, Cu, Fe, and Cd), talk presented at the Oct. 8-13, 1972, meeting of the Electrochemical Society in Miami Beach, Florida.

70. Maienthal, E. J., Analysis of Sb-Bi, Cu-Ni-Cr-Al, and Pb-Sn-Te thin films, Polarographic Analysis, 29, NBS Tech. Note 455, Taylor, J. K., ed., (1968).

71. Yana, M., Mochizuki, H., Kajiyama, R., and Koyama, Y., Polarographic determination of arsenic in iron and steel, Japan Analyst, 5, 160-3 (1956).

72. Dolezal, J., and Novak, J., Rapid methods for analysis of metals and mineral raw materials, (Cu and Bi), Collect. Czechoslov. Chem. Communs., 24, 51 (1959).

73. Scholes, P. H., An evaluation of the formate buffer method for the simultaneous determination of Cu and Pb in steel, Analyst, 86, 116-24 (1961).

74. Tajima, N., and Kurobe, M., Determination of traces of copper and lead in cast iron and pig iron, Japan Analyst, 9, 801-6 (1960).

75. Stabryn, J., Polarographic determination of copper, zinc and chromium in cast-iron turnings, Hutn. listy, 15, 302 (1960).

76. Nadezhina, L. S., and Razumova, V. P., Polarographic determination of small amounts of lead in pure metals and ferrous alloys, Zhur. Anal. Khim., 12, 731-5 (1957).

77. Goto, H., and Namiki, M., Simultaneous determination of Pb and Zn in iron, steel and iron ores, by D. C. polarography, Sci. Dept., RITU, 19, 245-53 (1967).

78. Yakovlev, P. Ya., Malinina, R. D., Razumova, G. P., and Dymova, M. S., Use of polarography in the analysis of ferrous metals (Sn, Pb, Cd, Cu, Sb, Bi, Ni, Co, Zn, and W), Teoriya i Praktika Polyarograf. Analiza, Akad. Nauk Moldavsk, SSR, Materialy Pervoga Vses. Soveshch, 1962, 198-202.

79. Scholes, P. H., The determination of tin in pure iron, mild steel and certain low-alloy steels by cathode ray polarography, Analyst, 86, 392-9 (1961).

80. Maekawa, S., Yoneyama, Y., and Fujimori, E., Determination of trace elements in iron and steel. I. Determination of zinc in iron and mild steel by dithizone extraction followed by polarography, Japan Analyst, 9, 244-7 (1960).

Pb and Pb-Base Alloys

81. Athavale, V. T., Dhaneshwann, R. G., Nehta, M. M., and Sundaresam, M., Polarographic determination of antimony in refined lead, Analyst, 86, 399-401 (1961).

82. Kraus, R., and Novak, J. V., Polarographic determination of Sb in hard Pb, Die Chemie, 56, 302-3 (1943).

83. Goto, H., and Ikeda, S., Polarographic determination of As in Pb, Sci. Rep. Res. Inst. Tohoku Univ., 9, 91-6 (1957).

84. Gertseva, N. S., Polarographic determination of bismuth, copper and lead when present together, Trudy Inst. Metallurg, Akad. Nauk, SSSR, 1957, 238-240.

85. Maienthal, E. J., Bismuth, In, Tl, and Cd in Pb-base alloys, Polarographic Analysis, 11, NBS Tech. Note 273 (1965).

86. Burlacu, G., Bot, O., and Antonescu, I., Polarographic determination of copper, lead, cadmium and zinc in lead concentrates, Stud. Cercet. Stiint. Chim., Cluj, 7, 17-23 (1956).

87. Zagorski, Z., Polarographic determination of oxidised lead in metallic lead, Chem. Anal., Warsaw, 1, 80-90 (1956).

88. Zagorski, Z., and Kempinski, K., Concentration of Ag traces in Pb by coprecipitation, Chem. Anal., 4, 423 (1959).

89. Shinagawa, M., Murata, T., and Yoshida, T., Polarographic determination of tin in lead-base alloy containing antimony, Japan Analyst, 6, 215-9 (1957).

90. Kovalenko, P. N., and Lektorskaya, N. A., Polarographic determination of tin and antimony in metallic lead, Zavod. Lab., 16, 924-9 (1950).

Ni and Ni-base Alloys

91. Korshunov, I. A., Suzanova, L. N., and Shchennikova, M. K., Polarographic determination of copper and iron in crude and cathode nickel, Zavod. Lab., 13, 569-71 (1947).

92. Yakovlev, P. Ya., Razumova, G. P., and Malinina, R. D., Polarographic determination of impurities in nickel-based alloys by co-precipitation with methyl violet, (Bi, Pb, Cd, Zn), Zavod. Lab., 25, 1039-41 (1959).

93. Mukhina, Z. S., Tikhonova, A. A., and Zhemchuzhnaya, I. A., Determination of traces of lead, bismuth, tin and cadmium in nickel-base alloys, Zavod. Lab., 22, 535-7 (1956).

Ores

94. Morris, A. G. C., Determination of traces of antimony, copper and lead in ferromanganese with a cathode-ray polarograph, Analyst, 87, 478-84 (1962).

95. Cerny, A., Indirect polarographic and complexometric determination of very small amounts of arsenic in iron and ores, Hutn. Listy, 13, 715-6 (1958).

96. Oshman, V. A., and Chistyakova, A. P., Polarographic determination of cadmium in an acid sulphate - iodide supporting electrolyte, Zavod. Lab., 27, 532-36 (1961).

97. Martynova, L. T., and Sochevanov, V. G., Polarographic determination of Cd in ores, Zavod. Lab., 26, 792-3 (1960).

98. Shcherbov, D. P., and Guzhova, E. P., The polarographic determination of cadmium and zinc in copper ores, Ref. Zhur. Khim., 1956, abstract no. 32,761.

99. Yonezaki, S., Polarographic analysis of metals. III. Rapid determination of copper in iron ore, pyrite cinder, and sintered ore; IV. Rapid determination of copper, antimony, lead, cadmium, nickel, zinc, cobalt and iron in Babbit metal, V. Determination of zinc on galvanized iron, Nippon-Kinzoku-Gakkai-Shi., 16, 581-4 (1952).

100. Borlera, M. L., Polarographic analysis of iron ores, (Cu, Mn, Pb, As, S, and Zn), Ric. Sci., 27, 1492-9 (1957).

101. Rooney, R. C., Polarographic determination of trace elements in Fe, J. Polarographic Soc., 1958, 21-4.

102. Scholes, P. H., Cathode-ray polarography: typical applications to metallurgical analysis, R. & D., 1962, 38-41.

103. Odone, G., and Picasso, G., Polarographic analysis of traces of metals in iron ores, (Cu, Pb, Zn, Ni, and Sn), Chim. e Ind., 42, 598-605 (1960).

104. Semerano, G., and Gagliardo, E., Polarographic determination of iron, lead, and zinc in some zinc ores, Anal. Chim. Acta, 4, 422-7 (1950).

105. Zelenina, T. P., Polarographic determination of lead in chromite ores, Sb. Trud. Vses. Nauch.-Issled. Gorn. -Metaluurg. Inst. Tsvet. Met., 1962, 335-8.

106. Aref'eva, T. V., and Vasil'eva, L. N., Polarographic determination of selenium and tellurium in complex ores and products of their working, Sb. Trud. Gos. Nauch.-Issled. Inst. Tsvet. Met., 1962, 669-75.

107. Alimarin, I. P., Ivanov-Emin, B. N., and Pevzner, S. M., Trudy Vsesoyuz. Kinferentsii Anal. Khim., 2, 471-92 (1943).

108. Kral, S., and Rett, V., Rapid polarographic determination of tin in ferrotungsten, metallic tungsten and tungsten ores, Hutn. Listy, 15, 638-9 (1960).

109. Shinagawa, M., Murata, T., and Okashita, H., Polarographic analysis of uranium. Separation of concomitant ions with anion-exchange resin, Japan Analyst, 8, 356-61 (1959).

110. Kral, S., and Kysil, B., Polarographic determination of very small amounts of zinc in ferromanganese and in manganese ores containing cobalt, Hutn. Listy, 13, 716-7 (1958).

111. Vesela, M., Polarographic determination Zn in Mn, ferromanganese and Mn ores, Hutn. Listy, 15, 805-6 (1960).

112. Ringbom, A., and Torn, L., Polarographic determination of small quantities of zinc in materials rich in iron, Finska Kemistsamfundets Medd., 56, 12-7 (1947).

113. Cooper, W. C., and Mattern, P. J., Polarographic determination of small amounts of metals in iron pyrites, (Zn, Cu, Ni), Anal. Chem., 24, 572-6 (1952).

Te and Te Concentrate

114. Pats, R. G., and Semochkina, T. V., Polarographic determination of lead and copper in tellurium and tellurium concentrate, Zavod. Lab., 28, 800-1 (1962).

Sn and White Metal Alloys

115. Itsuki, K., and Kaji, T., Determination of copper and lead in crude tin by alternating current polarography, Japan Analyst, 8, 568-71 (1959).

116. Pats, R. G., Tsfasman, S. B., and Semochkina, T. V., Determination of Cu, Pb, Cd, and Zn in white metallurgy products on an a.-c. polarograph, Zavod. Lab., 29, 395-401 (1963).

117. Faucherre, J., and Souchay, P., Polarographic determination of traces of metals in alloys containing large quantities of tin, lead, and antimony, (Cu, Fe, Bi, Cd, Ni, Zn), Bull. soc. chim. France, 1949, 722-8.

118. Huang, H., Rapid (polarographic) determination of traces of zinc in tin alloys, Hua Hsueh Tung Pao, 11, 52 (1962).

TiO_2

119. Lagrou, A., Vanhees, J., and Verbeek, F., Determination of traces of Sb, Cu, and Pb in TiO_2 by pulse polarography, Z. anal. Chemie., 224, 310-17 (1967).

U

120. Saito, K., and Takeuchi, T., Determination of trace impurities in metallic uranium. XIV. Determination of lead by alternating-current polarography, Japan Analyst, 10, 152-6 (1961).

Zn and Zn base Alloys

121. Gajan, R. J., and Geehan, D. M., Rapid determination of aluminum, iron, copper, cadmium and lead in zinc-base alloys, Rep. Invest. U. S. Bur. Mines, 5727, 10 pp. (1961).

122.Ensslin, F., Dreyer, H., and Abraham, K., The polarographic determination of Cd and Tl in the presence of one another, Metall u. Erz, 39, 184-7 (1942).

123. Pletenev, S. A., and Aref'eva, T. V., Determination of cadmium and copper in zinc sulfate solution by the polarographic method, Trudy Vsesoyuz. Konferentsii Anal. Khim., 2, 451-5 (1943).

124. Kemula, W., Rubel, S., and Zakrzewska, G., Polarographic determination of copper and iron in the presence of a large excess of zinc, Chem. Anal., Warsaw, 8, 51-8 (1963).

125. Provaznik, J., and Mojzis, J., Application of inversion polarography for the determination of microgram quantities of lead in zinc, gallium, antimony and arsenic, Chem. Listy, 55, 1299-1303 (1961).

126. Seith, W. and vor dem Esche, W., The polarographic determination of trace elements in zinc, (Pb, Cd, Tl, Bi, Sn), Z. Metallkunde, 33, 81-2 (1941).

127. Baev, F. K., Polarographic determination of Pb and Tl impurities when present in Zn salts and Zn, Uch. Zap. Rostovsk Univ., 40, 163-72 (1958).

128. Hawkings, R. C., Simpson, D., and Thode, H. G., The polarographic determination of tin in high-purity zinc and zinc die-casting alloys, Can. J. Research, 25B, 322-40 (1947).

129. Sietnieks, A. J., The polarographic determination of small amounts of tin in zinc die-casting alloys, Acta Chem. Scand., 6, 1217-22 (1952).

Reviews

130. Rooney, R. C., Polarographic determination of trace elements in Fe, J. Polarographic Soc., 1958, 21-4.

131. Scholes, P. H., Cathode-ray polarography: typical applications to metallurgical analysis, R. & D., 1962, 21-4.

132. Milner, G. W. C., Application of the polarograph to metallurgical analysis. I. Determination of trace elements in zinc and zinc alloys, Metallurgia, 33, 321-3 (1946).

C. Slurry Streams, Feeds to and from Flotation Processes, Sediments in Flotation Processes, and Water (general).

133. Proszt, J., and Gyorbiro, K., Polarographic testing of drinking and usable water. I. Determination of hardness and alkali-metal content. (K, Na, Ca, and Mg), Chem. Anal. Warsaw, 1, 21-8 (1956).

134. Proszt, J., and Gyorbiro, K., Polarographic investigation of potable water and of water for industrial use. The determination of hardness and of alkalis, (Ca, Mg. and Na+K), Anal. Chim. Acta, 15, 585-91 (1956).

135. Reznikov, A. A., and Starik-Smagina, A. S., Polarographic determination of sodium and lithium in natural waters, Trudy Vsesoyuz, Konferentsii Anal. Khim., 2, 559-72 (1943).

136. Vancells, L. E., and Casassas, E., Polarographic determination of magnesium in presence of calcium with 2,2' dihydroxyazobenzene. Application to analysis of waters and calcareous materials, Inform. Quim. Analit. Pura Apl. Ind., 24, 1-14 (1970).

137. Nicolson, N. J., The application of pulse polarography in analysis for some metal ions in water (Al, Cu, Pb and Fe), Tech. Memo. Wat. Res. Ass., TM59, 22 pp. (1970).

138. Hodgson, H. W., and Glover, J. R., Polarographic determination of aluminum, zinc, and tin in water, Analyst, 76, 706-10 (1951).

139. Mal'kov, E. M., Fedoseeva, A. G., and Stromberg, A. G., Determination of nanogram amounts of antimony or bismuth [in natural water] by anodic-stripping voltammetry after their separation by extraction, Zh. Analit. Khim., 25, 1748-51 (1970).

140. Whitnack, G. C., and Brophy, R. G., A rapid and highly sensitive single-sweep polarographic method of analysis for As (III) in drinking water, Anal. Chim. Acta, 48, 123-7 (1969).

141. Oliver, H. R., Polarography of arsenic in the mineral waters of La Bourboule, Bull, Soc. Chim. Biol., 36, 695-703 (1954).

142. Rozanski, L., Indirect polarographic determination of arsenate in mineral waters, Chemia Analit., 16, 793-799 (1971).

143. Davidyuk, L. A., New polarographic determination of As in natural H_2O, Dopov. kad. Nauk Ukr. RSR, (1966), 90.

144. Mal'kov, E. M., and Fedoseeva, A. G., Determination of nanogram amounts of bismuth [in natural water] by anodic stripping [from a mercury-graphite electrode], Zavod. Lab., 36, 912-14 (1970).

145. Souabni, A. Es and Nangniot, P., Determination of traces of cadmium, cobalt, copper, iron, manganese, lead and zinc in Belgian mineralised natural waters by differential oscillopolarography under an imposed voltage, Chim. Analyt., 53, 176-182 (1971).

146. Odier, M., and Plichon, V., Copper in solution in sea water: chemical form and determination. Study by a.c. polarography, Anal. Chim. Acta, 55, 209-220 (1971).

147. Kuroda, K., The copper content of the hot springs of Yunohanazawa, Hakone, Kanagawa Prefecture, and that of the hot springs of Osoreyama, Aomori Prefecture, Bull. Chem. Soc. Japan, 16, 69-74 (1941).

148. Reznikov, A. A., Polarographic determination of small quantities of copper, bismuth, lead, cadmium, and zinc in natural waters, Trudy Vsesoyuz. Konferentsii Anal. Khim., 2, 573-84 (1943).

149. Sinko, I., and Dolezal, J., Simultaneous determination of copper, cadmium, lead and zinc in water by anodic-stripping polarography, J. Electroanal. Chem., 25, 299-306 (1970).

150. Chizhevskaya, M. S., The polarographic determination of copper in industrial effluent waters, Sb. Nauch. Rabot, Molotov Med. Inst., Molotov, 1955, 79-82.

151. Whitnack, G. C., Applications of cathode-ray polarography in the field of oceanography. (Cu, Co, Zn, Mn, J. Electroanal. Chem., 2, 110-115 (1961).

152. Abdullah, M. I., and Royle, L. G., Determination of copper, lead, cadmium, nickel, zinc and cobalt in natural waters by pulse polarography, Anal. Chim. Acta, 58, 283-8 (1972).

153. Ullmann, W. W., Pfeil, B. H., Porter, J. D., and Sanderson, W. W., Voltammetric determination of metals in low concentrations [in trade wastes] (Cu, Pb, Ni, Zn, and Cd), Anal. Chem., 34, 213-6 (1962).

154. Canals, E., Marignan, R., and Cordier, S., Polarographic analysis of thermal waters. I. Construction of a laboratory polarimeter (Cu Ni and Co), Trav. Soc. Pharm. Montpellier, 8, 57-60 (1948).

155. Porter, J. D., Ullman, W. W., Sanderson, W. W., Purdue Univ., Eng. Bull., Ext. Ser., 1959, 587. (Publ. 1960) (Cu, Zn, Cd, Pd, and Ni in trade wastes).

156. Samuel, B. W., and Brunnock, J. V., Polarographic method for parts per billion [U.S.] of copper and lead in catalytic reformer feedstocks, Anal. Chem., 33, 203-5 (1961).

157. Virf, L., and Makai, V., Identification and determination of traces of copper, zinc and cobalt in mineral waters by polarography, Stud. Univ. Babes-Bolyai, Cluj, Chim., 8, 221-4 (1963).

158. Kuroda, K., Lead content of the hot springs of Japan, Bull. Chem. Soc. Japan, 15, 153-5 (1940).

159. Buchanan, E. B., Jr., Schroeder, T. D., and Novosel, B., Square-wave polarographic deterination of lead as a pollutant in river water, Anal. Chem., 42, 370-3 (1970).

160. Pohl, F. A., A quick determination method of trace elements (ppb range) in the reactor water, Z. Anal. Chem., 197, 193 (1963).

161. Bonsels, W., Linnemann, F., and Pohl, F. A., Automated analysis of very pure water (Al, Bi, Cd, Co, Fe, Ga, In, Ni, Pb, V, Zn, Zr), Z. Anal. Chem., 222, 210 (1966).

162. Kovalenko, P. N., Polarographic determination of small amounts of lead and cadmium in copper electrolytes (rapid method), Uch. Zap. Rostov. na Don Univ., 41, 123-134 (1958).

163. Wahlin, E., Polarographic determination of traces of metals in organic material. Determination of Pb, Cu, Cd, Ni, Zn and Fe, Acta Chem. Scand., 7, 956-68 (1953).

164. Visintin, B., Monteriolo, S., and Giuseppi, S. A., Polarographic determination of lead, cadmium, tin and zinc in water, Ann. Idrol., 1, 212-21 (1963).

165. Mal'kov, E. M., Fedoseeva, A. G., Slastenova, O. A., and Stromberg, A. G., Determination of traces of lead and copper [in natural waters and effluents] by anodic-stripping polarography on a mercury graphite electrode, Zavod. Lab., 36, 1439-41 (1970).

166. Weiss, D., and Fidler, J., Oscillopolarogrpahic determination of low concentrations of heavy metals in mine waters, (Pb, Cu, Ni, Cd, and Zn), Rudy, 12, 204 (1964).

167. Popova, T. P., Polarographic determination of lead and zinc in natural waters, Sh. Nauch. Tekhn. Inform. Min. Geol. i Okhrany Nedr., (1955) 129-30.

168. Tikhonov, M. K., and Shalimov, G. A., (Ni and Mn in Ocean H_2O), Gidrofiz. i. Gidrokhim. Issled., Akad. Nauk Ukr, SSR, (1965) 133.

169. Smith, J. D., and Redmond, J. D., Anodic-stripping voltammetry applied to trace metals in sea water (17 ions) J. Electroanal. Chem., 33, 169-75 (1971).

170. Cervenka, A., and Korbova, M., Polarographic determination of selenium in water, Chem. Listy, 49, 1158-61 (1955).

171. Antal, P., Sources of error in the polarographic determination of microgram amounts of uranium (after enrichment of solid samples and water), Mikrochim. Acta, 2, 235-44 (1961).

172. Spivakovski, V. B., Zimina, V. A., and Gavrilyuk, L. S., Determination of uranium traces in minerals and in natural waters, Zavod. Lab., 27, 390 (1961).

173. Koyama, K., Michelson, C. E., and Alkire, G. K., Automatic polarograph for continuous measurement of U in process waste streams, U. S. Atomic Energy Commission, HW-30148, (1953).

174. Alkire, G. J., Koyama, K., Hahn, K. J., and Michelson, C. E., Plant-type polarographic system for determining uranium in radioactive waste streams, Anal. Chem., 30, 1912-15 (1958).

175. Wilson, J. D., Webster, R. K., Milner, G. W. C., and Smales, A. A., A comparison of three methods of determining the concentration of uranium in sea water, Anal. Chim. Acta, 23, 505 (1960).

176. Milner, G. W. C., Wilson, J. D., Barnett, G. A., and Smales, A. A., J. Electroanal. Chem., 2, 25-38 (1961).

177. Hetman, J. S., Application of polarography to analysis of sewage and industrial wastes (V, Cr, Ni, Co, Ca, Mg, $S^=$, $SO_3^=$, $SO_4^=$, and CN^-), Proc. Effl. and Water Treatment Conv. (1960) 60.

178. Kuroda, K., Zinc content of the Hot Springs of Japan, Bull. Chem. Soc. Japan, 15, 88-92 (1940).

179. Macchi, G., Determination of ionic zinc in sea water by anodic-stripping voltammetry with use of ordinary capillary electrodes, J. Electroanal. Chem., 9, 290-98 (1965).

180. Ariel, M., and Eisner, U., Trace analysis by A.S.V. I. Trace metals in Dead Sea brine 1. Zn and Cd, J. Electroanal. Chem., 5, 362 (1963).

181. Whitnack, G. C., and Sasselli, R., Application of anodic-stripping voltammetry to the determination of some trace elements in sea water (Zn, Cd, Pb and Cu), Anal. Chim. Acta, 47, 267-74 (1969).

182. Muzzarrelli, R. A., Ricardo, A. A., and Laszlo, S., Chitosan for the collection from sea water of naturally occurring zinc, cadmium, lead and copper, Talanta, 18, 853-8 (1971).

183. Allen, H. E., Matson, W. R., and Mancy, K. H., Trace-metal characterization in aquatic environments by anodic stripping voltammetry, (Zn, Cd, Pb, Cu), J. Water Pollut. Contr. Fed., 42, 573-81 (1970).

184. Cravo, M. do Rosario, Polarographic determination of zinc and iron in natural water, Rev. Port. Quim., 10, 149-156 (1968).

Reviews

185. Maienthal, E. J., and Taylor, J. K., Electrochemical techniques in water analysis, in Water and Water Pollution Handbook, 4, 1751 Lili Ciaccio, ed., Marcel Dekker, N.Y. (1973).

186. "Polarographic methods in determination of trace inorganics in water," (Ca, Mg, Na, Li, Al, Zn, Sn, As, Cu, Cl, O, Bi, Cd, Br, I, F, U), Maienthal, E. J., and Taylor, J. K., in Trace Inorganics in Water, 172-82, Advances in Chemistry Series 73, (1968).

CHAPTER 9

POTENTIOMETRY (ION-SELECTIVE ELECTRODES)

Richard A. Durst

1. INTRODUCTION

Ion-selective electrodes, when applicable, provide one of the simplest analytical methods for measurement of the concentration of dissolved substances. Modern electronic potentiometers provide essentially direct readout in concentration units, independent of operator skill or judgment. When the substance of interest is already dissolved, it may be monitored automatically and continuously.

Selectivity is produced in an electrode by selection or suitable modification of the electrode membrane material. Thus the glass electrode which is highly selective for hydrogen ions and provides the best means for pH measurement, may be made responsive to other univalent cations by modification of the glass matrix. Selectivity for other ions is achieved by the use of electrodes incorporating solid membranes or by use of liquid ion-exchange membranes as electrodes. Background information on these and related matters will be found in the general references (1, 2).

A. General Considerations

Applicability to most of the sample matrices under consideration requires a pretreatment procedure involving sample dissolution and masking of interferences to provide an appropriate sample in solution form. In certain cases, process streams - including feeds, effluents, and slurries - may be monitored directly by electrode sensors with minimal pretreatment. Ion-selective electrodes are logarithmic sensors (emf output is proportional to the logarithm of the concentration) hence their response, i.e., precision, is constant over their entire dynamic operating range. Strictly speaking, the electrodes respond to ionic activities rather than concentrations. The latter, which is ordinarily the quantity of analytical interest, must be obtained by dividing the activity by the activity coefficient. This problem can be overcome by empirical calibration using solutions of known concentration. Dissolution of the sample in a medium of constant ionic environment is another procedure that has been used (1,2). Under ordinary laboratory conditions, an imprecision of approximately 1-5 percent is normal, while in plant or remote monitoring situations, 5-10 percent imprecision may be expected. Using titration procedures, which are usually more complex and time consuming than direct measurements, imprecisions on the order of 0.1 percent can be achieved. For routine analyses, automatic titrations and standard addition techniques using Gran plot end-point detection can result in rapid determinations while still retaining the higher accuracy and precision.

Manpower skills required to make electrode measurements are minimal once the analytical procedures are developed, however, sample preparation and pretreatment may be highly complex and require a technician trained in chemical manipulations such as wet ashing, separations, and dilution.

At the present time, there are over two dozen different kinds of commercially available ion-selective electrodes. Of these, almost half are suitable for the determination of elements of interest in this survey. The cost of these sensors range from $150 to $300, depending on type (i.e., solid-state, liquid ion-exchange, combination, etc.). Portable, battery-operated meters are available in the $300 to $500 range, while more sophisticated laboratory-based digital readout meters cost approximately $1,000. In addition, it is usually convenient to use a recorder ($300 to $2,000, depending on features) to monitor emf stability and plot titrations, although this accessory is not required. Other items such as stirrers, reagents, and glassware are usually trivial expenses. Thus, an ion-selective electrode measurement system can be acquired for as little as $500, or more typically, $1,000 to $2,000.

Analysis costs will depend on the number of samples to be analyzed, the pretreatment involved which depends on the matrix of the sample, and the accuracy and precision desired which determine the particular electrode procedure to be used, i.e., direct measurement, titration, addition technique, etc. In general, automated procedures can be developed based on electrode sensors.

2. APPLICATIONS

Ion-selective electrodes have not yet found extensive use in the analysis of the process materials surveyed in this report. On the other hand, they are being used in closely related situations such as for the analysis and monitoring of industrial wastes. Accordingly, it is reasonable to assume that they could provide advantageous methodology in selected applications. With this in mind, the characteristics of the presently available electrodes are summarized and references are given to applications that are related to, or have some aspects in common with the materials of interest to this report.

A. Cadmium

range: 10^{-1}M to 10^{-7}M (10 ppb).

pH range of operation: 1 - 14.

interferences: Ag^{+}, Hg^{++}, and Cu^{++} must be absent; Pb^{++} and Fe^{+++} must not exceed Cd^{++} level.

Applications include industrial wastes, plating solutions, non-ferrous alloys, and lubricating oils and greases (3).

B. Calcium range: 1M to 10^{-5}M (0.4 ppm).

pH range: 5.5 - 11.

interferences (in decreasing order of selectivity): Zn^{++}, Fe^{+++}, Pb^{++}, Cu^{++}, Ni^{++}, Sr^{++}, Mg^{++}, Ba^{++}.

Applications include monitoring of process stream water (hardness), calcium in food processing, and the calcium content of minerals (5, 6).

C. Copper range: 1M to 10^{-8}M (6 ppb).

pH range: 0 - 14.

interferences: Ag^{+} & Hg^{++} must be absent; Fe^{+++} must be less than 1/10 Cu^{++} level.

Applications include monitoring plating and etching baths for printed circuit manufacture, oil refining processes, industrial and mining waste waters, and determining copper in ores, minerals and alloys (7, 8).

D. Cyanide range: 10^{-2}M to 10^{-6}M (0.03 ppm).

pH range: 0 - 14.

interferences: sulfide ion must be absent; iodide should not exceed the cyanide level. To prolong electrode life, an operating range of 10^{-3}M to 10^{-5}M CN^{-} is recommended.

Applications include monitoring industrial metal extractions and certain petrochemical processes, determination of cyanide in plating baths, rinse tanks, and metal finishing solutions (9).

E. Fluoride range: 1M to 10^{-6}M (0.02 ppm).

pH range: 0 - 9.

interferences: hydroxide ion is the only significant interference: OH^- concentration must not exceed F^- level, i.e., pOH>pF.

Applications include monitoring municipal water supplies, electroplating baths, etching and cleaning solutions, pesticides, industrial waste waters, stack gases, and minerals (10-21).

F. Lead range: 10^{-1}M to 10^{-7}M (0.02 ppm).

pH range: 2 - 14.

interferences: Ag^+, Hg^{++}, and Cu^{++} must be absent from the sample; Cd^{++} and Fe^{+++} must not exceed the Pb^{++} level.

Applications include measurement of lead in electroplating baths, petroleum products, and non-ferrous alloys (22).

G. Silver/sulfide range: 1M to 10^{-7}M Ag^+ or $S^=$ (0.01 ppm Ag^+; 0.003 ppm $S^=$)

pH range: 0 - 14.

interferences: mercury is the only interference - must be absent from the sample solution.

Applications include measurements of silver or sulfide in industrial process streams and waste waters, e.g., free sulfide detection in the manufacture of paper and pulp (23, 24, 25).

H. **Sodium** range: 1M to 10^{-6}M (0.02 ppm)

pH range: 3 - 12.

interferences: the most serious interference is Ag^+ to which the electrode is 10^4 times more sensitive; H^+ is also a serious interference but easily controlled by pH buffering; Li^+, K^+, and NH_4^+ are minor interferences.

Applications include monitoring high-purity boiler water, pulping liquors, and the purification effectiveness of desalination plants (26, 27, 28).

I. **Potassium** range: 1M to 10^{-5}M (0.4 ppm).

pH range: 2 - 11.

interferences: major interference from Cs^+ and Rb^+; minor interference from NH_4^+, Na^+, Ag^+, and Li^+.

Applications include monitoring potassium in industrial process streams and in biological fluids (29, 30).

3. DISCUSSION

Ion-selective electrodes can be used to determine specific elements precisely and at very low levels if the matrices can be suitably modified or degraded to provide the elements as ions in solution. For most of the matrices under consideration in this survey, such a conversion can be carried out by chemical means, e.g., wet ashing with acids. This chemical pretreatment is time-consuming and often requires considerable skill but in many cases can be automated if large numbers of samples are to be processed.

Once the samples are in the appropriate solution form, the electrode determination is relatively simple and can be performed by a variety of techniques depending on the accuracy and precision desired. Using direct potentiometry or one of the single-increment techniques, imprecisions of 1 percent to 10 percent can be achieved by most electrodes, if interferences are properly masked, from concentrated solutions to the 1 ppm level. At the sub-ppm level, precision will degrade due to variable blanks, poor ionic buffering, and slower electrode response. Direct potentiometry or addition methods are rapid, requiring only 1 to 5 minutes and are easily portable for field use. For higher precision, 0.1 percent to 1 percent, titrations or multiple-addition techniques can be used with a concomitant increase in experimental complexity and time required for the analysis (3 to 15 minutes).

A wide range of sample sizes can be analyzed by electrode sensors with the upper limit defined only by homogeneity considerations. With miniaturized electrodes, lower sample volume limits of 1μl to 10μl are feasible. For a 10^{-5}M solution, only about one nanogram (10^{-9}g) of sample element is required. The feasibility of such microdeterminations has been reported, e.g., 0.4 ng of fluoride (10 μl) was determined with an accuracy and precision of about 1 percent using a fluoride electrode (31).

REFERENCES

(1) Durst, R. A., Editor, "Ion-Selective Electrodes," NBS Spec. Publ. 314, U.S. Govt. Printing Office, Washington, D.C., 488 pp, (1969).

(2) Moody, G. J., and Thomas, J. D. R., "Selective Ion Sensitive Electrodes," Merrow Publishing Company, Watford, England, 147 pp, (1971).

(3) Frant, M. S., and Ross, J. W., Alkaline Pulping Liquor Analysis, TAPPI 53, 1753 (1970).

(4) Frant, M. S., Application of Specific Ion Electrodes to Electroplating Analyses, Plating, 686, (1971).

(5) Woolson, E. A., et al., Soil Calcium Determination Using a Calcium Specific Ion Electrode, Soil Science 109, 279 (1970).

(6) Nakayama, F. S., and Rasnick, B. A., Calcium Electrode Method for Measuring Dissociation and Solubility of Calcium Sulfate Dihydrate, Anal. Chem. 39, 1022 (1967).

(7) Baumann, E. D., and Wallace, R. M., Cupric-Selective Electrode with Copper (II) - EDTA for End Point Detection in Chelometric Titrations of Metal Ions, Anal. Chem. 41, 2072 (1969).

(8) Frant, M. S. Applications of Specific Ion Electrodes to Electroplating Analyses, Plating, 686, (1971)

(9) Frant, M. S., et al., Electrode Indicator Technique for Measuring Low Levels of Cyanide, Anal. Chem. 44, 2227 (1972)

(10) Elfers, L. A., and Decker, C. E., Determination of Fluoride in Air and Stack Gas Samples by Use of an Ion Specific Electrode, Anal. Chem. 40, 1658 (1968).

(11) Plucinski, E. C., "Determination of Microgram Quantities of Fluoride in Metal Oxides," U.S. A.E.C. Report BNWL-601, (1968).

(12) Moeken, H. H., et al., The Potentiometric Determination of Fluorine in Nuclear Fuel Reprocessing Solutions, Anal. Chim. Acta 45, 233 (1969).

(13) Edmond, C. R., Direct Determination of Fluoride in Phosphate Rock Samples Using the Specific Ion Electrode, Anal. Chem. 41, 1327 (1969).

(14) Guth, J. L., and Wey, R., A Rapid Determination of Fluoride in Minerals and Rocks, Bull. Soc. Franc. Mineral. Crist. 92, 105 (1969).

(15) Collis, D. E., and Diggens, A. A., The Use of a Fluoride Responsive Electrode for "On-Line" Analysis of Fluoridated Water Supplies, Water Treatment and Examin. 18, 192 (1969).

(16) Pavel, J., et al., Microdetermination of Fluorine in Organic Compounds by Direct Measurement with a Fluoride Electrode, Microchem. J. 15, 192 (1970).

(17) Younghans, R. S., and McMullen, T. B., Fluoride Concentrations Found in NASN Samples of Suspended Particles, Fluoride 3, 143 (1970).

(18) Ficklin, W. H., "A Rapid Method for the Determination of Fluoride in Rocks and Soils, Using an Ion-Selective Electrode," U.S. Geology Survey Prof. Paper 700-C (1970).

(19) Buck, M., and Reusmann, G., A New Semi-Automatic Method for Fluoride Determination in Plant and Air Samples, Fluoride 4, 5 (1971).

(20) Rinaldo, P., and Montesi, P., Instrumental Techniques for Titration of Fluoride in Cryolite and Aluminum Fluoride, La Chemica e L'Industria 53, 26 (1971).

(21) Svoboda, K., and Ixfeld, H., Sampling and Automatic Analysis of Gas Forming Fluoride Emission, Staub-Reinhalt 31, 1 (1971).

(22) Frant, M. S., Application of Specific Ion Electrodes to Electroplating Analyses, Plating, 686, (1971).

(23) Swartz, J. L., and Light, T. S., Analysis of Alkaline Pulping Liquor with Sulfide Ion-Selective Electrode, TAPPI 53, 90 (1970).

(24) Muller, D. C., et al., Determination of Silver in Parts per Billion Range with a Selective Ion Electrode, Anal. Chem. 41, 2038 (1969).

(25) Brunow, G., et al., Reactions of Sulfur during Sulfate Pulping, Acta Chem. Scand. 26, 1117 (1972).

(26) Lenz, B. L., and Mold, J. R., Ion-Selective Electrode Method Compared to Standard Methods for Sodium Determination in Mill Liquors, TAPPI 54, 2051 (1971).

(27) Webber, H. M., and Wilson, A. L., The Determination of Sodium in High Purity Water with Sodium Responsive Glass Electrodes, Analyst 94, 209 (1969).

(28) Eckfeldt, E. L., and Proctor, W. E., Low Level Sodium Ion Measurement with the Glass Electrode, Anal. Chem. 43, 332 (1971).

(29) Frant, M. S., and Ross, J. W., Potassium Ion Specific Electrode with High Selectivity for Potassium over Sodium, Science 167, 987 (1970).

(30) Krull, I. H., et al., A Solid Potassium Ion Selective Electrode, Anal. Letters 3, 43 (1970).

(31) Durst, R. A., Fluoride Microanalysis by Linear Null-Point Potentiometry, Anal. Chem. 40, 931 (1968).

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16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

Various approaches to the chemical analysis of heavy industry process materials and effluents for trace element constituents that might contribute to environmental pollution are summarized.

The capabilities and costs of nuclear methods, spark source mass spectrometry, x-ray fluorescence and electron microprobe spectrometry, atomic absorption spectrometry, absorption spectrophotometry, atomic emission spectroscopy, voltammetry (polarography) and potentiometry (ion-selective electrodes) for determining traces (less than 100 parts per million) of mercury, beryllium, cadmium, arsenic, vanadium, manganese, nickel, antimony, chromium, zinc, copper, lead, selenium, boron, fluorine, lithium, silver, tin, iron, strontium, sodium, potassium, calcium, silicon, magnesium, uranium, and thorium in such matrices as fly ash, coal, oil, ores, minerals, metals, alloys, organometallics, incinerator particulates, slurry streams, and feeds to and from sedimentation processes have been assessed.

The report includes a critically selected bibliography of the current literature.

17. KEY WORDS (Alphabetical order, separated by semicolons)

17. KEY WORDS: Air pollution; atomic absorption; electron microprobe; emission spectroscopy; environmental analysis; industrial effluents; ion-selective electrodes; nuclear activation analysis; particulate analysis; polarography; spark source mass spectrometry; spectrophotometry; trace elements; water pollution; x-ray fluorescence.

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