
*Characterization of Solids—Chemical Composition**

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1. Introduction

In any series of studies, experimental or theoretical, in the chemistry, the physical chemistry, or the chemical physics of solids it is very important that there be reliable, descriptive, analytical information available about the materials used in the studies.^(1,2) Such information is obtained through the process called “characterization,” which has been given the following definition by the National Academy of Sciences—National Research Council Committee on Characterization of the Materials Advisory Board:⁽³⁾

“Characterization describes those features of the composition and structure (including defects) of a material that are significant for a particular preparation, study of properties, or use, and suffice for reproduction of the material.”

Only when optimal information is given on the identity and the location of the atoms in a particular material can one be confident that the material can be reproduced, and therefore that the measurements and theories involving this material will have lasting significance.

This principle is easy to accept as a general statement of philosophy. However, there are many examples of elaborate scientific studies in which it was belatedly discovered that the effects measured

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were a function of unknown impurities in the material, of surface phenomena, etc.

Selective characterization of materials used in studies of properties is essential because composition and structure effectively determine the properties of materials. However, chemical analysis, i.e., the determination of chemical composition, can present a bewildering maze of information to the materials investigator interested in obtaining basic characterization data. He needs perspective as to the possible utility of different types of analytical techniques so that he can make intelligent decisions as to the analytical approaches that will be most significant for his problems.

It is this perspective that this chapter is designed to furnish. The Report of the Materials Advisory Board Committee⁽³⁾ presented an integrated summary of pertinent information on many analytical techniques that can be used in determining the composition of solids.* Unfortunately, the report has had only limited distribution and its information is now somewhat dated.

This chapter is modeled after the MAB Report, updating and expanding the coverage to correspond to the state of the art in January 1973. A short description of various analytical techniques used to obtain composition information on materials is followed by a tabular summary of sensitivities and precisions of these techniques. The next section describes the application of these techniques to specific characterization problems such as stoichiometry, homogeneity, and oxidation state, as well as survey and quantitative methods of measuring impurities. Finally, examples are given from the literature of detailed studies on a number of high-purity materials to illustrate the present state of the art of characterization of practical samples.

2. Current Capability for Determination of Chemical Composition

2.1. Introduction

Any meaningful discussion of current capabilities in the measurement of composition must focus on the real world of practical materials.

* The original members of the Panel on Composition of the MAB Committee that prepared this report were: M. S. Sadler, DuPont, Chairman; R. A. Laudise, Bell Laboratories; R. J. Maurer, University of Illinois; W. W. Meinke, National Bureau of Standards; and A. Wold, Brown University.

In 1933 G. E. F. Lundell, then the Chief Chemist of the National Bureau of Standards, wrote a very candid article entitled, "The Chemical Analysis of Things as They Are."⁽⁴⁾ He said he used that title because so many articles on analysis appearing in the literature dealt with the "chemical analysis of things as they are not."

Much the same problem exists in the materials analysis field today. The scientific literature contains numerous references to materials of 5-9's and 6-9's purity. Such statements are misleading and of questionable validity because the estimates are in many cases derived from resistivity measurements supplemented by emission spectrographic analyses (with a sensitivity of only 1–10 ppm for most elements). To establish that a sample of material contained less than 1 ppm total impurities would require analyses for all elements present by techniques with sensitivities and accuracies in the range 1–20 ppb.

The magnitude of effort required is illustrated by the classic work on zone-refined aluminum by Albert of the CNRS Laboratory in Paris.⁽⁵⁾ Samples were analyzed for over 60 elements plus the rare earths by high-sensitivity neutron activation using detailed radiochemical procedures. Elements such as carbon, oxygen, and nitrogen were determined by photonuclear or charged-particle activation. This procedure required the efforts of a four-man team for 12 hr, an additional person for nine days, and another person for two weeks to analyze the rare earths. After the amounts of individual contaminants were totaled (for many there were only experimental upper limits of 1–10 ng), it was possible to establish that a particular sample of aluminum contained less than 2 ppm total impurities (i.e., it was not quite 6-9's pure).

Unfortunately, little confidence can be placed in most general statements of purity, such as 6-9's. It is imperative that analytical information be developed from more discriminating techniques.

2.2. General Overview

The following sections contain short summaries of a number of different analytical techniques that are useful in the determination of chemical composition. The first techniques include those that usually require dissolution of the sample, with measurements being made on the resulting solutions. Then techniques that can be applied directly to the sample with or without some modification of the sample itself

are described. Finally, techniques that provide chemical structure information as well as information on the localization of elements and on surfaces are discussed. The major emphasis is on the analysis of inorganic materials, although a number of techniques that give information on the rapidly developing field of organic materials have also been included.

For each section several definitive references enable the reader desiring more information to go directly to authoritative literature that describes the technique and defines some of its important characteristics and limitations.

There are several general references that are applicable to many of the areas described. Kolthoff and Elving's *Treatise on Analytical Chemistry*⁽⁶⁾ is a many-volume work that treats in detail most of the individual techniques described in the chapter as well as many applications of these techniques of interest to the materials scientist. The proceedings of the first NBS Institute for Materials Research Symposium on Trace Characterization, Chemical and Physical⁽⁷⁾ contains a number of definitive papers. Furthermore, each year the journal *Analytical Chemistry* publishes a set of reviews in many areas of analytical chemistry that should be consulted for information on specific materials problems. In the even years these appear as fundamentals reviews,⁽⁸⁾ while in the odd years they are applications reviews.⁽⁹⁾

Although a serious attempt has been made to be selective and candid in the references, the reader should be aware that measurements at or near the limits mentioned may prove very difficult unless the analyst has had considerable experience in applying the method to the matrix described.

Experience at NBS in the certification of high-purity Standard Reference Materials has illustrated the point that on most real samples, trace element analysis below the ppm level gives values of questionable accuracy.^(10,11) All trace methods of analysis except activation analysis must deal realistically and directly with problems of "blank" contamination, i.e., contamination introduced into the sample through preliminary handling and/or subsequent processing in the analytical procedure.

Furthermore, interpretation of the analytical results must include critical consideration of the "sampling" procedure, e.g., how representative the analyzed sample is of the total material being used for materials studies.

2.3. Analytical Techniques: Present Status

2.3.1. Wet Chemistry—Classical Gravimetry and Titrimetry

Gravimetry,^(12,13) or quantitative analysis based on the weight of a reaction product, is the oldest of the analytical techniques and one of the most useful for major and minor constituents. It is capable of high accuracy, especially when corrections for solubility are made. Much of the early atomic weight work, with precisions as high as 0.001 %, was based on this technique.

Titrimetry,^(12,13) or quantitative analysis based on the amount of a standard solution consumed in a reaction, is another valuable technique for the analysis of both major and minor constituents. It is capable of high accuracy, especially when the amount of reagent consumed is determined by weight, and in such cases accuracies of 0.01 % have been obtained. Volumetric titrimetry can readily yield results of 0.1 % accuracy.

Classical gravimetric and titrimetric procedures based on reactions in aqueous or liquid media have been designated as “wet chemical methods” to distinguish them from instrumental analytical methods. In a recent discussion of the criteria for the development of gravimetric methods it was pointed out that, with some exceptions, it is difficult to find an instrumental method that does not use classical analyses to provide the compositions of standards required for calibrating the instruments.⁽¹⁴⁾

The relatively high accuracy of these gravimetric methods stems from the ability to assess systematic errors from theoretical equilibria calculations,⁽¹⁵⁾ and from the relatively small corrections applied to the final weighed products. Present-day automated balances have greatly simplified the weighing process. Gravimetric methods, when applied to the newer radiochemical, stable-isotope mass spectrometric, and other instrumental methods, play a significant role in current analytical procedures for chemical characterization of a wide variety of materials. The continuous growth in use of these techniques arises from the extensive applications of complexometric reactions that assure greater specificity.^(16,17)

Titrimetric (or volumetric) methods depend on the detection of an “end point” of the stoichiometry of a reaction. Strictly interpreted, the classical methods are limited to visual indicators of the end point. There are, however, other instrumental modes that include a variety of electrometric, spectrophotometric, spectrofluorimetric, and enthalpic techniques. These latter methods are also amenable to

automation and computer interfacing. As indicated in the literature,^(18,19) this field offers selective and sensitive methodology for major and trace components of many different materials.

2.3.2. Coulometry

Coulometric measurement involves the quantitative electrochemical conversion of a constituent in solution from one initial oxidation state to another, well-defined oxidation state. The quantity measured is the charge necessary to perform this conversion. Since electrons are essentially being used as the measured reagent, this method is capable of high precision and accuracy.

In an electrolysis system the conversion can be performed in two experimentally controlled modes: controlled-potential mode and constant-current mode. In the former case one selects the potential to be maintained at such a value that only the desired reaction can proceed. In the second mode, the constant-current mode of electrolysis, a “depolarizer” introduced into the electrolysis system reacts at the electrode to produce a titrant for the species in question. Thus the name “coulometric titration” has been attached to this mode of electrolysis.

Coulometry can be classified as a macro method, involving grams of sample.⁽²⁰⁾ The use of submilligram samples in coulometry, on the other hand, classifies it equally well as a micro method.⁽²¹⁾ High-precision coulometry has been widely used for the determination of major constituents of various materials.⁽²²⁾ Determination of trace impurities, e.g., dopants such as chromium in ruby lasers, has been performed at the nanogram level.⁽²¹⁾ It has been used successfully for the determination of stoichiometry of materials such as GaAs,⁽²³⁾ for measurement of physical constants such as the faraday⁽²⁴⁾ and atomic weights,⁽²⁵⁾ for determination of major constituents of Standard Reference Materials,⁽²⁶⁾ and for the analysis of important research materials such as separated isotope solutions.

2.3.3. Ion-Selective Electrodes

Ion-selective electrodes^(27,28) can be used for analytical determinations over an extremely wide range of solution concentrations (from 10^{-5} to 10^{-7} M to saturation) and are therefore applicable to trace as well as to major-constituent analysis. There are presently about two dozen ion-selective electrodes commercially available for cations, including the heavy metals; for anions such as fluoride, sulfide, and the halides; and for gases such as oxygen, carbon dioxide, and ammonia.⁽²⁹⁾

These sensors are usually used in one of two operational modes, direct potentiometry or potentiometric titrations. Direct potentiometry (similar to a *pH* determination with a *pH* meter), which is based on the correlation of the electrode emf to a standard or calibration curve, is normally limited to a precision of, at best, 0.5%. It is, nonetheless, a technique that is very simple, rapid, and convenient to use.

Greater precision can be attained with a titration procedure but with a concomitant increase in experimental sophistication. Typically, precisions on the order of 0.1% are achieved, while under optimum conditions this may be improved by one order of magnitude. A titration procedure has an additional advantage in that the number of species that can be determined is greatly increased by using indirect titration methods.

A good, working knowledge of wet chemical procedures, solution equilibria, and electrode limitations is necessary for the reliable application of these sensors to analytical problems. Although analogous to electrometric *pH* determinations in theory and in operation, ion-selective electrodes are considerably more subject to chemical interferences and prone to nonideal behavior.

2.3.4. Polarography

This versatile solution technique^(30,31) covers the entire concentration spectrum from trace quantities through major constituent levels. In principle, any element capable of electrooxidation or electroreduction can be determined, and the polarographic behavior of some 80 elements has been described. Polarographic half-wave potentials are ordinarily sufficiently different to make possible the simultaneous determination of several elements in the same solution, thus minimizing the need for pre-separations in many instances. Sensitivities in the range 0.1–0.001 ppm have been reported, depending upon whether conventional or modified techniques such as cathode-ray,⁽³²⁾ pulse, or anodic stripping⁽³³⁾ polarography are employed. Precision near the limit of detection is about 20%, increasing to about 2% in favorable concentration ranges. Differential techniques that have been developed make possible the determination of microamounts of major constituents with standard deviations of 0.02–0.05%.⁽³⁴⁾ Polarographic techniques have made important contributions to the trace analysis of a number of reference materials, including trace glass samples,⁽³⁵⁾ lunar samples,⁽³⁶⁾ and botanical samples.⁽³⁷⁾

2.3.5. Spectrophotometry

Absorption spectrophotometry is one of the most widely used analytical techniques for solutions. For example, of the 10^9 clinical analyses made in the U.S. in 1972 more than 90% used spectrophotometry as the final measurement step. It is used in many laboratories for trace analysis⁽³⁸⁾ because of its simplicity, modest apparatus requirements, sensitivity, and good precision (1–5%). Although it is primarily a trace method, differential techniques also permit the determination of major constituents with a relative standard deviation of 0.1%. By the use of photon counting,⁽³⁹⁾ a precision of 0.01% should be attainable.

While in most cases the color reactions used are not specific, numerous procedures can be made selective by the proper choice of pH and the addition of masking agents. Recent developments^(40,41) in double-wavelength spectrophotometry have further increased the specificity of many direct methods. Separation and preconcentration techniques can be applied, but these impose a restriction on the detection limit based on the reproducibility and magnitude of the blank. Theoretical and practical considerations presently set the limit of detection on the most sensitive spectrophotometric methods at 5–20 ng.

In addition to the analysis of solutions, spectrophotometry has also found unique applications in the nondestructive determination of doped impurities in single crystals such as, for example, the determination of chromium in ruby.⁽⁴²⁾

2.3.6. Spectrofluorimetry

Since the 1950's fluorescence has enjoyed increased use and acceptance as an analytical measuring tool because of increased instrumental refinements and the method's inherent sensitivity and selectivity. High detection sensitivity results from the fact that the signal-to-noise ratio is large and can be electronically amplified, while selectivity results from the fact that either the emission or excitation spectra can be used to characterize the fluorescing species. In addition, analytically useful information such as sample purity, concentration, metal oxidation state, and number of binding sites can be obtained from consideration of quantum efficiencies and lifetime and polarization measurements.

This is a rapidly developing field.⁽⁴³⁾ Analytical procedures can be established by several methods: specie fluorescence; fluorescence quenching; chemically induced fluorescence (e.g., chelation of non-fluorescent metal ions with fluorescent ligands); and enzymic reactions that produce fluorescent products.⁽⁴⁴⁾ Sample concentrations and identities can be determined in solution, on powders, or on glasses.

Fluorimetry is essentially a trace method, since the emitted light is proportional to specie concentrations only at low concentration levels (10^{-4} – 10^{-9} M). Concentration quenching usually occurs at higher levels, and linearity is destroyed. At the limits of detection, fluorescence can be drastically affected by the presence of fluorescing impurities, by any process which quenches fluorescence, or by interferences by Raman or Rayleigh scattering.

Microspectrofluorimetry is also being used to determine luminescence in heterogenous systems such as powders⁽⁴⁵⁾ or cells,⁽⁴⁶⁾ with an ultimate sensitivity on the order of 10^{-14} g of material.

2.3.7. Organic Microanalysis

Microanalysis, the detection and identification of materials present in small size but relatively high concentration, is distinct from trace analysis, which is concerned with the characterization of small concentrations of material. Organic microanalysis is usually taken to mean elemental analysis (primarily C, H, O, N, P, S, Cl, Br, I, and Si), and functional group analysis (acetyl, carboxyl, benzoyl, amino, nitro, hydroxy, etc.) on samples usually 1–10 mg in size. The semiquantitative results, accurate to about 10%, serve as a measure of impurities, or inhomogeneity, or for structure determination in solid organic substances. Accurate results of 1% or better may be expected when large (1 g) samples are taken for analysis and the entire chemical apparatus is scaled upward in size. However, small samples take less time to analyze, so the micro methods are more popular than macro methods.

Recent texts^(47,48) describe modern methods for organic elemental and functional group analysis that still depend heavily on classical wet chemical procedures. Automated instruments are now available for laboratories with heavy work loads of routine C, H, O, and N analyses. A rapid, semiquantitative analytical procedure for organic functional groups and for inorganic elements in organic and inorganic materials is afforded by the Weisz ring-oven.⁽⁴⁹⁾ This is an instrument for separating the components in a drop (0.05-ml) of solution, in much the

same way as in thin-layer and paper chromatography. The separated components are not in the form of spots, however, but are concentrated into sharp lines by a heated platen (the oven) that evaporates the solvent and deposits all the solute at one specific location on the paper or other chromatographic substrate for further handling. Ring-oven separations of organic materials may be followed by color spot tests,⁽⁵⁰⁾ or the rings containing the solutes may be removed from the substrates, as in thin-layer chromatography, and characterized by sensitive instruments.

The identification of a completely unknown organic substance is a very difficult undertaking because of the very large number of different organic materials presently known. Most often there is at least a partial knowledge of the composition of the material, and additional information on purity or structure is needed. Then organic microanalysis can help complete the picture.

2.3.8. Thin-Layer Chromatography (TLC)

This semiquantitative method for the analysis of mixtures of nonvolatile organic or inorganic substances combines a simple means for separating the constituents of the dissolved mixture with their detection by the application of chemical and physical tests.⁽⁵¹⁾ If the mixture contains unknown substances, identification can be made by molecular characterization of extracted constituents; somewhat less assurance is afforded through correlations with the TLC behavior of known compounds.

In practice, TLC can be used to analyze 300–1000 μg of a mixture applied to the plate as a single spot. The chemical and physical properties of each separated constituent, or those of the variety of products into which the constituent may be converted to enhance detection, provide its limit of detection. In favorable cases as little as 10–30 μg of a compound may be detected; commonly the limit is 100–1000 μg ; occasionally more. Preconcentration of specific constituents of a mixture by liquid chromatography or thick-layer (preparative) chromatography can provide improved sensitivity.

Quantitative analysis may be performed directly on the thin-layer plate in a variety of ways: by visual comparison; by measurement of spot areas; by the transmittance of spots that are colored, are charred, or that absorb ultraviolet light; by reflectance; or by fluorescence. Alternatively, the zone of absorbent containing the constituent can be scraped from the plate and extracted. The extract is then analyzed by

any of a variety of techniques appropriate for the substance. An extensive variety of organic and inorganic materials has been studied by TLC, and recent compendia^(51,52) provide excellent sources of reference to specific applications.

2.3.9. Gas Chromatography*

This technique⁽⁵³⁾ assumes that the sample components of interest may be volatilized, have a vapor pressure of 0.1 mm or greater at a temperature less than 400°C, and are thermally stable at that temperature. In this manner, major and minor components for both organic and inorganic analyses can be separated and analyzed. The range of analysis nominally extends from major components to impurities present in concentrations as low as 10^{-12} g. Solids, liquids, and gases with molecular weights from 2 to 200,000 may be analyzed, although special sampling techniques may be required for nonvolatile compounds. These techniques include derivatization,⁽⁵⁴⁾ pyrolysis,⁽⁵⁵⁾ and indirect analysis of reaction products.⁽⁵⁶⁾ The time required for gas chromatographic separations is normally a few minutes; however, sample separation, quantitative data reduction, and sample identification usually extend the total analysis time to several hours, depending upon the complexity of the sample.

Chemical characterization by gas chromatography is usually directed toward trace organic analysis. The accuracy of the analysis is limited by the sampling and injection procedures, chromatographic resolution, detector calibration, peak area measurements, and the availability of known standards. The relative precision is highly dependent upon the analyst's experience and understanding of the technique and on the concentration level being determined. The best possible precision that can be obtained under the most favorable conditions is 0.1 % for major components in near-ideal samples, increasing to ≥ 10 % below the 10 ppm level.⁽⁵⁷⁾

Identification of chromatographic effluents is most definitively accomplished by coupling to a mass spectrometer. Virtually every instrumental method of analysis, however, has been employed either on-line or off-line for peak identification.

2.3.10. Liquid Chromatography

High-performance liquid chromatography is emerging as a "new" separation and analysis technique for the characterization of volatile

* A more correct designation is "gas-liquid chromatography."

and nonvolatile components.⁽⁵⁸⁾ The emphasis is directed primarily toward organic analysis because of the many potential applications in the analysis of complex materials. The sample must be soluble in a nonreactive, nonviscous solvent for separation on the basis of adsorption, partition, ion exchange, or molecular size.

The moving or mobile phase is a liquid of well-defined composition and is pressurized to 500–3000 psi in order to force the sample through 1-m columns. The chromatographic column is packed with particles ranging in diameter from 5 to 100 μm and analyses can be carried out in a few minutes for pesticides or in a few hours for urine separations. Stable and tailored column materials have only recently become available and are directly responsible for the resurgence of interest in liquid chromatography.⁽⁵⁹⁾ However, these materials are expensive (\$5–\$500 per column) and special low-volume (10 μl) detector cells are required. Analysis and detection is primarily by UV or differential refractive index measurement. These detectors are not particularly sensitive, and auxiliary methods are required for identification. Lower limits of detection for the UV detector depend on the molar absorptivity of the analyte.⁽⁶⁰⁾ Many compounds may be measured with this detector in the ppm to 0.001 ppm concentration range, while others will be best analyzed by the refractive index detector, with a lower limit of detection of approximately 1 ppm. This sensitivity may be extended by a judicious choice of mobile phase.

2.3.11. Activation Analysis

This technique^(61–63) is particularly useful for ultra-trace analysis of solid samples in that it eliminates most of the problems of reagent “blanks” and/or sample contamination during analysis.⁽¹¹⁾ The large number of variables (such as type and energy of irradiating particle, time of irradiation and measurement, type of detector used, etc.) that can be judiciously altered for particular analyses make the technique relatively free from serious systematic errors or biases. A typical value for the random errors is $\pm 5\%$ at the 100-ng level.

The use of high-resolution Ge(Li) gamma-ray detectors allows limited nondestructive multielement analysis, but when the number of elements determined is large (> 10) precision and accuracy for many of the elements may be expected to suffer ($> \pm 20\%$). This nondestructive approach,⁽⁶⁴⁾ i.e., “activation spectrometry,”⁽¹¹⁾ usually requires two or more separate irradiations with corresponding decay periods prior

to measurement of up to 30 days or even longer for some matrices. This long analysis time is unacceptable for many applications.

Many laboratories employ radiochemical separation techniques to isolate groups of elements from the sample after irradiation. The combination of simple group separations and high-resolution gamma-ray spectroscopy reduces substantially the analysis time and analytical costs, and makes the technique nearly a true “multielement” method. Additional effort is being expended to automate these group separations to further decrease analytical costs.

Activation analysis with neutron generators (fast neutrons) provides a nondestructive method for the determination of oxygen at the 10–100- μg level. Carbon, nitrogen, and oxygen can be determined in submicrogram quantities with high-energy photons⁽⁶⁵⁾ (bremsstrahlung from electron linear accelerators, LINAC's) although no useful nitrogen determinations have been demonstrated in practical matrices. The short half-life (124 sec) of ^{15}O makes this measurement difficult, and methods development for a given matrix is necessary before the method can be applied routinely. Carbon analyses have been performed routinely with the LINAC, with excellent sensitivity and accuracy.

Activation analysis with charged particles, although essentially a surface technique, has been used to determine carbon, nitrogen, and oxygen, especially in high-purity silicon,⁽⁶⁶⁾ and offers excellent sensitivity and good reliability when done carefully.

2.3.12. Vacuum Fusion, Inert Gas Fusion, and Extraction

The effects of trace amounts of interstitial elements (H_2 , O_2 , and N_2) on the chemical and physical properties of materials have been widely recognized. From among the many techniques—activation analysis, mass spectrometry, spectroscopy, wet chemical, vacuum fusion, and inert gas fusion—the latter two have probably found widest application. Horton and Carson⁽⁶⁷⁾ describe advances in instrumentation for solid samples that have increased the daily output from a few samples to 60 samples. This in turn permits better evaluation of the experimental parameters and leads to the improvement of precision. However, the accuracy is still dependent upon the availability of appropriate standards.⁽⁶⁸⁾ Furthermore, when the concentration of gases is very low, below 1 ppm, one must distinguish carefully between that portion present on the surface and that in the bulk of the material.⁽⁶⁹⁾ Systems with computer-controlled interfacing

have recently been described⁽⁷⁰⁾ that provide fully automated analysis.

2.3.13. Thermal Analysis

Thermal analysis gives information on the fundamental behavior and structure of materials based on their thermochemical and thermophysical properties. Differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetry (TG), dilatometry, and other related dynamic thermal methods serve as analytical tools for characterizing a wide variety of solid materials.⁽⁷¹⁾ Information obtainable by these methods includes phase relationships, identification and measurement of impurities in high-purity materials, “fingerprint” identifications, thermal histories of the material, and dissociation pressures.

Thermogravimetry offers accurate measurements of reactions involving weight changes and can be used in assessing the purity of materials. On the other hand, DTA measurements can be made to closely approximate the thermodynamic conditions of a process and elucidate the mechanism of reactions. Proceedings of several recent conferences,^(72–74) as well as review articles,⁽⁷⁵⁾ describe a wide range of applications, from fundamental thermodynamics and kinetics to industrial process control.

2.3.14. X-Ray Fluorescence Spectrometry

This technique^(76,77) is useful for the determination of major and minor constituents in solid samples with a typical sensitivity of 20–200 ppm, depending upon the atomic number of the element and the nature of the specimen. In favorable cases, or when preconcentration methods are used, the sensitivity may be extended to as low as 0.1 ppm.⁽⁷⁸⁾ Commercial instruments are available for analysis with X-ray wavelengths shorter than 10 Å; these permit the determination of any element heavier than sodium (atomic number 11).

The precision of X-ray spectrometric analysis (0.1% in good cases; more typically 0.5%) is frequently competitive with quantitative “wet” chemical analysis and often superior to other “instrumental” techniques. For X-ray analytical techniques to be accurate, standards of composition close to that of the samples, or suitable correction procedures for any existing interelement effects, must be available. X-ray analysis is widely used in industry because of its accuracy and

because it lends itself to automated measurements and data evaluation procedures. Of additional advantage, it is usually rapid and often nondestructive. Samples that can be analyzed cover a broad range, including alloys, powders, solutions, slag, slurries, and ores.⁽⁷⁹⁾

With the development of solid-state detectors of improved resolution, the application of energy-dispersive X-ray fluorescence analysis, using radioisotope or X-ray tube excitation, is extending rapidly. Sensitivities of a few ppm on simple matrices (e.g., organic materials) have been obtained.⁽⁸⁰⁾ The energy-dispersive method offers economical means of analysis for a wide range of materials, including metals, ores, and solid atmospheric pollutants.

2.3.15. Spark Source Mass Spectrometry (SSMS)

This instrument can detect ~85 elements at concentrations as low as 1–10 ng/g. Conducting and semiconducting solids are the ideal sample forms.⁽⁸¹⁾ Powders, insulators, liquids, etc. can also be analyzed with various techniques, but with possible loss in sensitivity and/or introduction of contamination. Interferences between elements will exist for all samples, depending on the elements present and their concentrations. The precision of an SSMS analysis at the 1 $\mu\text{g/g}$ concentration level is $\pm 5\text{--}20\%$ for photographic detection and $\pm 2\text{--}5\%$ for electronic detection.⁽⁸²⁾

The accuracy of an analysis can approach these values when Standard Reference Materials of the same matrix are available or when a synthetic standard can be applied. In the absence of standards, concentrations can be estimated to within a factor of 3–10 of the true value. This method of analysis is ideal for a general survey covering all possible trace elements. The results of such survey analyses can then be used to assign the analysis of specific impurities to other trace techniques when more accurate values are required.

2.3.16. Isotope Dilution—Spark Source Mass Spectrometry

Isotope dilution analysis with the SSMS can be used with almost all of the polynuclidic elements. Accuracies of $\pm 5\text{--}10\%$ are obtained on 0.1–1 μg of a trace element using photographic detection,⁽⁸³⁾ better accuracies should be obtainable with electronic detection. Analysis of trace impurities at 0.01 ng/g concentrations has been possible⁽⁸⁴⁾ using SSMS isotope dilution on samples amenable to preconcentration techniques. Isotope dilution requires dissolution of samples before the

separated enriched isotope (spike) of each element being determined is added and equilibrated. Chemical separation steps are then required to obtain the elements in a measurable form. However, since this technique is capable of determining many elements in a single sample simultaneously (~ 17 elements in acids), general group separations can be used.⁽⁸⁴⁾

2.3.17. Isotope Dilution Mass Spectrometry

The availability of separated isotopes in the late 1940's made possible analyses by isotope dilution mass spectrometry.⁽⁸⁵⁾ Geologists were the first to capitalize on the new tool, and by the mid-1950's the field of geochronology was well established. Extremely precise and accurate concentration determinations down to the sub-ppm level are required for meaningful age calculations.

Geologists and lunar scientists now use this technique to measure not only elements like lead, uranium, thorium, rubidium, strontium, argon, and potassium, but they also now include barium and ten of the rare earths in geologic analysis. The nuclear industry measures lithium, boron, uranium, and plutonium routinely. The technique has a potential for broad application. Major and minor phases of such elements as molybdenum (55 %) and rhenium (0.1 %) can be determined because accuracy is possible even in the presence of major interferences. At impurity levels of 1–500 ppm almost all of the above-mentioned elements can be determined, and, in addition, such elements as magnesium, chromium, copper, silver, calcium, nickel, and cesium.^(36,86,87)

It is possible to analyze approximately 40 elements by thermal ionization mass spectrometry and another ten elements by electron impact (including gaseous compounds of elements such as nitrogen, oxygen, carbon, and silicon). When isotope dilution is applicable, it usually is by far the most accurate method for the determination of impurities and traces. The leverage for precision and accuracy comes from the limited number of quantitative steps necessary for the analysis.

Certification of the elements important to geochronologists in the NBS Trace Glass Standard Reference Materials⁽³⁵⁾ has been accomplished in large part by this technique. Measurements of these elements at the 500-ppm level are certified at an accuracy of $\sim 0.2\%$; at the 50-ppm level at an accuracy of 0.2–0.5%; at the 1-ppm level at an accuracy of 0.2–0.8%; and at the 0.02-ppm level at an accuracy of

1.5–3.0%. Such measurements, especially at the lower two concentrations, require extreme care, special clean facilities, special clean reagents and containers, and a large amount of time and effort.⁽¹¹⁾

2.3.18. Emission Spectroscopy

Qualitative analysis by emission spectroscopy^(88,89) permits rapid, simultaneous detection of some 70 metallic and metalloid elements. Only a few milligrams of a solid sample are required. An estimate of the concentration of an element, often within one order of magnitude or somewhat better, can be made from intensities of the spectral lines. The experimental limit of detection of each element depends on the nature of the sample, the excitation procedure, and the properties of the spectrograph and detector.⁽⁹⁰⁾ Detection limits cited in the literature range down to nanogram levels for many elements. However, on complex practical samples few reliable quantitative measurements below the 1–10 ppm level are reported in the literature.

Recent developments with controlled spark discharges, induction-coupled plasmas, capillary arcs, and laser excitation have considerably expanded the capabilities for quantitative analysis by emission spectroscopy.⁽⁹¹⁾ The detection of nonmetallic elements, including carbon, nitrogen, oxygen, and the halogens, has been reported, often at concentrations as low as 10 ppm.⁽⁸⁸⁾

The unavailability of suitable standards can severely restrict the quantitative applications of this method. For some sample forms standards can be prepared from the sample by the method of additions. Preconcentration methods that utilize chemical separation are also useful for spectrographic analysis; these methods facilitate the preparation of standards because the matrix has been simplified. On the other hand, such preconcentration methods or the preparation of standards by the method of additions increase the likelihood of contamination of the sample. “Common matrix” methods, involving dilution of the samples with a material such as germanium or gallium oxide, are not applicable to the analysis of the purest materials, since the dilution process raises the limits of detection.

2.3.19. Flame Emission, Atomic Absorption, and Atomic Fluorescence Spectrometry

These three spectroscopic methods^(92–95) employ rather similar equipment, and some commercial apparatus offers interconvertibility.

The methods are complementary in that elements with poor detection limits by one technique can often be determined with high sensitivity by the other. They also share many problems, particularly with respect to interferences.

The sensitivity of detection of some 70 elements by flame emission or absorption spectrometry can, in many instances, be very low.^(96,97) The level of detection of sodium by flame photometry is often limited by the residual content of the water or other solvent used for the sample; e.g., 1 ng/g of sodium can be detected without difficulty. Detection limits reported for other elements range from 1 to 1000 ng/g by one or the other of these two techniques. The potential capabilities of these methods have been considerably improved by the introduction of nonflame techniques.⁽⁹⁸⁾

All of these methods require that the sample be dissolved, which necessarily causes some dilution and a consequent loss of sensitivity. In addition, matrix effects can cause serious error unless standards similar in composition to the sample can be prepared. The use of organic solvents, rather than water, often improves the limits of detection, occasionally by an order of magnitude or more; flame emission and absorption measurements are often especially useful in the determination of impurities following solvent extraction.

Atomic fluorescence signals have been observed for 35 elements in flame and nonflame devices, and preliminary work⁽⁹²⁾ indicates that this method may provide very low limits of detection. Matrix effects may, however, cause difficulties in the analysis of practical samples.

2.3.20. Mössbauer Spectroscopy

This analytical method^(99,100) has been used to great advantage in the determination of chemical structure.⁽¹⁰¹⁾ It complements the other hyperfine interaction spectroscopies (such as nuclear magnetic resonance) in several ways. The technique observes the changes in two energy levels within the nucleus as a function of chemical environment, as contrasted to changes in the ground state only, e.g., in NMR. The Mössbauer technique, in contrast to NMR, is primarily used in the solid state. The broadening of NMR spectra caused by solid-state interactions is absent in Mössbauer spectroscopy because recoilless emission in Mössbauer spectroscopy demands no solid-state (phonon) interaction.

The technique has proven to be a powerful tool for measuring properties such as magnetic and electric field interactions in the solid

state.⁽¹⁰²⁾ It has also proven useful in the fields of metallurgy, solid-state physics, coordination chemistry, and biochemistry, and in the theory of the hyperfine interaction.

At present the elements with which this effect can be observed with high practicability are limited to iron, tin, iodine, gold, and a few rare earths.

The inherent excitation linewidth guarantees specificity of elemental detection. Most Mössbauer measurements have been made on materials in which the Mössbauer resonating element is a macroconstituent in the matrix. Some work has been done in which the matrix investigated constitutes the source of excitation for Mössbauer spectroscopy and in this sense constitutes an analysis of a trace impurity in the matrix.⁽¹⁰³⁾

2.3.21. Nuclear Magnetic Resonance (NMR)

NMR is a well-established method^(104–106) for identifying and studying structure of molecules in the liquid state. Since solids are in general characterized by broad resonance lines with little fine structure, application of NMR to the characterization of solids with respect to composition is limited and highly specialized. Sensitivity varies with the kind of nucleus but generally does not exceed 10^{19} nuclei/cm³ or 0.1 at. %.

In metals with cubic lattice symmetry, determinations of impurities at concentrations of 0.1 at. % have been made using quadrupole interactions and changes in the Knight shift. Another approach involves study of the coupling between the nuclear spin system and the lattice through measurement of the spin–lattice relaxation time.^(107,108) In nonmagnetic solids paramagnetic impurities affect the relaxation time dramatically, and these effects can be detected for impurities in the 10–100-ppm range. However, these latter methods are not specific for a single impurity but are influenced by valence, size, or some other property that may be common to a number of impurities.

2.3.22. Electron Spin Resonance (ESR)

This technique⁽¹⁰⁹⁾ is useful for studying conduction electrons in metals and semiconductors as well as bonding of transition metal ions and other paramagnetic species. In general, it is more suitable for determination of environment than for identification of elements and measurement of concentration. Sensitivity varies with the para-

magnetic species, and for transition elements under optimum conditions is in the range of 10^{10} spins/cm³. Therefore it can be used to detect trace impurities in special cases; e.g., free radicals in an organic matrix⁽¹¹⁰⁾ or transition metals in a diamagnetic solid.⁽¹¹¹⁾

2.3.23. Residual Resistance Ratio (RRR)

This method⁽¹¹²⁾ measures the sum of the “electrically active” elements and is highly sensitive. It does not identify impurities, and different impurities affect residual resistance in varying degrees; some contaminants have little or no appreciable effect. RRR finds wide application in the characterization of metals,^(113,114) but from an analytical viewpoint it is of value primarily to check the consistency of other analytical data for high-purity materials.

2.3.24. Electron-Probe Microanalysis

In many types of solid samples the distribution of the elements present is as important as the average composition. This is particularly true for many alloys, minerals, ceramics, and semiconductor devices. The development of the electron probe, capable of investigating the distribution (on the μm scale) of all elements of atomic number above five at concentrations as low as 0.1 %, and frequently 0.01 %, permits studies of microstructure to an unprecedented degree.⁽¹¹⁵⁾

The localization of structural features in the electron probe is aided by scanning techniques⁽¹¹⁶⁾ that produce electron microprobe images of small sectors of the sample surface. It is also possible to obtain scanning images of element distribution. The most attractive feature of electron probe microanalysis is the fact that a quantitative analysis is possible, with errors of less than 3 % relative in most cases.^(117,118) Data evaluation requires the use of a computer, but the operation can be performed in a time-share mode, or even on line with a small computer, and pure elements or simple compounds can be used as reference materials.

The in-depth resolution of the electron probe is about the same as the lateral resolution (1–3 μm). Normally, the analysis is restricted to regions as large or larger than these dimensions. However, the instrument is employed increasingly in the characterization of films of submicrometer dimensions, (determining both film thickness and composition⁽¹¹⁹⁾) as well as of small particles. A search of the literature shows that the electron probe has been applied to a wide range of materials.⁽¹²⁰⁾

2.3.25. Ion-Probe Microanalysis

The limitations in sensitivity and in depth resolution of the electron-probe microanalyzer prompted the development of ion-probe microanalysis. This technique⁽¹²¹⁾ is based on mass spectrographic analysis of the secondary ions emitted from a sample under the impact of a focused and accelerated primary ion beam. This type of analysis also offers, in comparison with the electron probe, the possibilities of isotopic analysis and the investigation of elements of low atomic number, including hydrogen, at trace concentrations.

Although the lateral resolution of the ion beam is similar to that of the electron beam (1–3 μm), the investigation of even a few atomic layers is possible.⁽¹²²⁾

By gradual erosion of the sample with a primary beam, a sensitive investigation of surface layers and of distribution in depth of impurities can be performed. It has been possible, for instance, to demonstrate the enrichment of traces of aluminum in the *p-n* junction of a silicon transistor device.

The sensitivity of the method, for many elements and samples, is in the ppm range. The analysis of nonconductors is possible when negative primary ions are employed. Therefore the method can be applied to a wide range of materials, including metals and alloys, oxidized alloy surfaces, semiconductors, ceramics, and minerals.

The possibility of quantitative analysis with the ion probe is presently a matter of controversy. Although theories have been developed that aim to predict the strong matrix effects inherent in this technique and to correct for them, further work is required before the efficacy of these procedures of data evaluation can be definitely assessed.⁽¹²³⁾ It is possible with calibration procedures, however, to obtain information on individual particles of micrometer size.⁽¹²⁴⁾

2.3.26. Photoelectron Spectroscopy

A very useful technique for determining the electronic states at the surface is photoelectron spectroscopy.^(125,126) Photon excitation of a surface from induced X-ray emission in materials such as magnesium or aluminum produces photoelectrons with energy sufficient to escape from depths of not more than a few atomic layers. Moreover, those electrons that escape without energy loss have an energy linewidth sufficiently narrow to allow observation of differences in chemical binding of the order of 0.1 eV.⁽¹²⁷⁾ This means that in many materials differences in chemical structure on the surface can be observed.

Alteration of the photoexcitation energy can produce other types of electron emission (such as the Auger effect) which result in a modified spectrum of the emitted electrons, thereby providing a “different look” at the energy levels in a chemical structure.⁽¹²⁸⁾ All of these techniques combine to provide a total picture of the surface structure.

2.4. Precision and Sensitivity of Analytical Techniques

The precision, the sensitivity, and the area of application of the techniques described in the previous sections are summarized in Table 1.

3. Application of Current Techniques to Characterization of Materials

3.1. Characterization of Major Phase

3.1.1. Stoichiometry

Classical wet chemical techniques based on gravimetry, titrimetry, and electrochemistry are most commonly used for major element analyses and stoichiometry, i.e., the relative ratio of the elements in a compound. Conventional gravimetric and volumetric methods^(12,13) are used for determinations at $\sim \pm 0.1\%$, and with refinements such as homogeneous precipitation, solubility correction, and the use of weight burettes, precisions can be extended to $\pm 0.01\%$. The most precise determinations of stoichiometry have been based on constant-current coulometry, where reliability at the 0.001–0.01% level can be obtained. For example, Marinenko⁽²³⁾ has determined the ratio of gallium to arsenic in single-crystal gallium arsenide to $\pm 0.007\%$, using constant-current coulometric determinations for both elements.

With X-ray fluorescence stoichiometry can be determined to ± 0.01 – 0.1% when suitable standards are available. Precise lattice parameters and pycnometric density determinations have been used to determine deviations from stoichiometry or nonstoichiometry in Bertholide-type compounds.⁽¹⁵¹⁾ Other instrumental techniques such as nuclear magnetic resonance and comparison of ferroelectric Curie temperatures have also found applications.⁽²⁾

TABLE 1
Precision and Sensitivity of Analytical Techniques

Technique	Applications	Sensitivity ^a	Precision	References
Wet chemistry gravimetry	Major- and minor-phase concentration	100 mg to 1 g 1–10 mg	0.003–0.01 % 0.1 %	15, 129 15, 129
Wet chemistry titrimetry	Major- and minor-phase concentration; also impurities	10 ⁻² M in solution 10 ⁻⁵ M in solution 10 ⁻⁶ –10 ⁻⁷ M in solution	0.01 % 0.1 % 0.2–1.0 %	15, 16, 129, 130 15, 16, 129, 130 15, 16, 129, 130
Coulometry	Major-phase concentration	—	0.001–0.005 %	20, 22, 26, 131
Ion-selective electrodes (direct)	Major- and minor-phase concentration; also impurities	10 ⁻³ M-saturation in solution 10 ⁻⁵ –10 ⁻³ M in solution <10 ⁻⁵ M in solution	0.5–2 % 1–5 % 2–30 %	27, 132 27, 132 27, 132
Polarography	Impurities, major and minor constituents	All in solution: 10–100 ppm 0.1–10 ppm 0.001 ppm (with anodic stripping preconcentration)	0.1–2 % 2–10 % 5–10 %	34 37 33
Spectrophotometry	Impurities	10–100 ppm in solution 0.005–0.1 ppm in solution	1–5 % 5–10 %	133–135 133–135
Spectrofluorimetry	Impurities; organic Impurities; inorganic: Rare earths Non rare earths	0.002–10 ppm 1–10 ⁴ ppm 0.001–10 ppm	0.5–20 % 1–50 % 1–10 %	45, 46 45, 46 45, 46
Organic micro-analysis	Major-phase impurities	10 μg	± 0.6 %	47, 136

TABLE 1 (continued)

Technique	Applications	Sensitivity ^a	Precision	References
Thin-layer chromatography	Minor constituents, trace impurities	10-1,000 µg	5-50%	51
Gas chromatography	Major- and minor-phase concentrations; also impurities; organic analysis	Major component 1-10% 0.1-1% 0.01-0.1% 10-100 ppm <10 ppm	0.1% 0.2-0.5% 0.5-1% 1-5% 5-10% ≥10%	53, 57 53, 57 53, 57 53, 57 53, 57 53, 57
Liquid chromatography	Major- and minor-phase concentration; organic analysis	0.001-1 ppm	1-20%	58, 137
Activation analysis	Impurities: Individual with } radiochemistry } Nondestructive (survey)	0.1-10 ppm 0.001-0.01 ppm 0.1-10 ppm	2-5% 2-10% 10 to >20%	62-64, 138 62-64, 138 62-64, 138
Vacuum fusion-mass spectrometry	Impurities: O ₂ N ₂ , H ₂	0.07 ppm 100 ppm	20% 5%	139, 140 139, 140
Thermal analysis	Change of phase; Impurities	10-100 µg	1-15%	71, 141, 142
X-ray fluorescence spectrometry	Major and minor constituents	20-200 ppm generally; 0.1 ppm with preconcentration	0.1-0.5% 2-10%	76, 77 78

Characterization of Solids—Chemical Composition

Technique	Applications	Sensitivity ^a	Precision	References
Spark source mass spectrometry	Impurities (survey)	0.001–0.1 ppm	5–20%	81, 82
Spark source mass spectrometry; isotope dilution	Impurities	10^{-5} –0.1 ppm	5%	83, 84
Isotope dilution mass spectrometry	Major- and minor-phase concentration; Impurities	500 ppm–100% 1–500 ppm 0.00001–1 ppm	0.1–0.2% 0.2–0.5% 0.5–50%	35 35, 36, 86 35, 36, 86
Emission spectroscopy	Impurities (survey)	0.1–100 ppm	5–10%	88, 90, 143
Flame emission	Impurities	0.1–10 ppm in solution 0.002–0.1 ppm in solution	0.5–5% 5–10%	92, 93, 95 92, 93, 95
Atomic absorption	Impurities	0.1–10 ppm in solution 0.005–0.1 ppm in solution	0.5–5% 5–10%	92, 93, 95 92, 93, 95
Atomic fluorescence	Impurities	0.1–10 ppm in solution 0.001–0.1 ppm in solution	2–5% 5–15%	92, 95, 144 92, 95, 144
Mössbauer spectroscopy	Major-phase valence; also impurities valence	Down to 0.0001–0.1% depending upon density of matrix	Semiquantitative now	145, 146, 147
Nuclear magnetic resonance	Major- and minor-phase concentration; Impurities	10^{-4} M in solution	1%	148

TABLE 1 (concluded)

Technique	Applications	Sensitivity ^a	Precision	References
Electron spin resonance	Impurities	0.001–1 μg	Semiquantitative now	110, 149, 150
Residual resistance ratio	Impurities (survey integral)	10^{-9} g	1–5%	113, 114
Electron probe microanalysis	Microscopic; homogeneity of major phases and minor phases	0.01–0.1% over a 1–5 μm scan diameter	0.5%	115, 117, 118
Ion probe microanalysis	Microscopic; traces, surface layers	1 ppm	Semiquantitative now	123
Photoelectron spectroscopy	Surface analysis of major phase	0.1%	5%	—

^a Provided purified reagents and clean room facilities are used. See note of caution in text.

3.1.2. Homogeneity (Including Impurity Distribution)

In addition to determining the *presence* of impurities in solid solution, it is also important to study the *distribution* of such impurities. The importance of knowing how the impurities are distributed, whether completely statistically at the atomic level or in a single “inclusion,” is vital to every interpretation of properties measured on the phase. In this field, the last ten years have brought a step-function advance with the introduction of the electron microprobe.⁽¹¹⁵⁾ Yet, even here spatial resolution is limited to about 1 μm , and sensitivity and precision are sometimes insufficient.

In some cases, cathodoluminescence in the probe provides a tool for detecting inhomogeneities at the ppm level with micrometer resolution. The scanning electron microscope, used judiciously, can provide (in favorable cases) data on impurity distribution at the 0.1- μm level. Here the ion probe holds promise both of sensitivity increased by a hundredfold and of sampling a few atom layers deep.

3.1.3. Oxidation State

Once exact stoichiometry has been determined it is conventional to represent the oxidation state (valence) of a multivalent element in a compound by rounding off to the nearest whole number and assigning formal charges so as to preserve electrical neutrality. This presents difficulties when more than one multivalent element is present in the same compound or when several oxidation states are possible for a given element in the compound, e.g., iron in magnetite, Fe_3O_4 .

If it is possible to dissolve the compound without altering the oxidation states, the classical wet chemical techniques of gravimetry, titrimetry, and electrochemistry can define the oxidation state to a precision of about 0.01 %. For some materials, such as $\text{K}_2\text{Cr}_2\text{O}_7$, such dissolution is possible with no measurable change in oxidation state to at least one part in 100,000. For other materials there is at least a partial change in oxidation state on dissolution, and one must resort to instrumental methods. For iron, tin, iodine, gold, and some rare earths Mössbauer spectroscopy is applicable with a precision of about 0.1 %.⁽²⁾ High-resolution X-ray spectra have also been used to determine oxidation state.

3.2. Characterization of Minor Phases and Impurities

Many impurities can be detected at the 1–10 ng/g level in simple systems. However, the limit of quantitative determination in practical

samples is generally much higher. The accuracy of quantitative analysis by many instrumental methods is frequently limited by a lack of suitable standards. Detection and determination of organic impurities in an organic matrix is an especially difficult problem.

3.2.1. Survey Methods

Emission spectroscopy is the most generally applicable of the survey methods although there are limitations on its sensitivity. It is widely used for characterization of solids, powders, liquids, and gases and has the capability of detecting up to 70 elements by direct current arc excitation. Determination of nonmetallic elements is also possible with emission spectroscopy, but this requires special techniques that are infrequently used.

Spark-source mass spectrometry can detect all elements, with sensitivities often as good as 1 ng/g. Residual gases in the vacuum system restrict detection limits for carbon, oxygen, and nitrogen to 0.1–1 $\mu\text{g/g}$.

X-ray spectroscopy can also be employed for survey analysis of impurities and has the advantage of being nondestructive. Lower limits of detection are rarely better than 10–100 ppm, unless preconcentration is used, and the elements of the first period cannot be detected at low concentrations.

Electrical measurements are useful for determining the total content of electrically active impurities in conductors and semiconductors. The shape of the freezing curve gives considerable information on total impurities in a material with a suitable melting point. Special techniques must be used for most metals that melt at high temperatures⁽¹¹⁴⁾ or for materials that decompose on melting.

Gas chromatography is a useful survey technique for organic analysis because a very broad range of samples may be characterized very quickly with columns that are nonpolar (for fixed gases and aliphatics), of intermediate polarity (for aromatics), and highly polar (for alcohols and esters). High-pressure liquid chromatography should be regarded as a complementary organic survey technique since it separates high-molecular-weight compounds. Ionic, polymeric, and thermally labile compounds may be separated by this method, although its sensitivity is presently limited to the μg range.

3.2.2. Quantitative Methods

Many of the techniques listed in Section 2.3 under analytical techniques and summarized in Table 1 can be applied to the quantita-

tive determination of impurities. The most serious limitations of these methods are the relatively poor detection limits for some, the need for standards of similar composition for the more sophisticated instrumental methods, and the hazard of contamination in methods that require preliminary dissolution and/or considerable handling or preparation of the sample.

Activation analysis is especially suitable for trace characterization, since most of the sample handling occurs after the activation step, and contamination problems are minimized. Equipment and operational costs, although high, are comparable to those required of many modern analytical techniques.

Spectroscopic methods (emission, mass, X-ray) are useful for determination of many elements in small absolute amounts, but are limited in the amount of sample that can be analyzed; they are also useful methods for determining groups of elements after chemical separation or preconcentration. These techniques (except for isotope dilution procedures) are limited by the availability of suitable standards.

Most of the other methods listed in Section 2.3 are restricted to the determination of a single element or a few elements at a time; they are most useful when there is critical interest in specific contaminants in the samples.

Organic impurities in organic matrices can frequently be separated by thin-layer chromatography, paper chromatography, liquid chromatography, or gas chromatography and can be determined by integration of the detector response curves. Detection limits depend heavily on the nature of the organic materials and impurities and on the signal/noise ratio of the chromatographic or spectroscopic method used to resolve the impurities or their signals. With practical samples detection limits are usually no better than 10 ppm.

The various techniques that give information on oxidation state and location all suffer from relatively poor sensitivity and are therefore more suitable for the characterization of the major phase than of the impurities. Magnetic resonance techniques (NMR and ESR) have low limits of detection, but both are limited in applicability.

Homogeneity of the sample is often a limiting factor in the analysis for a trace constituent.

3.3. Characterization of Surfaces

Undoubtedly, among the least understood and most poorly characterized features of a solid is the surface. Electronic "mapping"

of solid surfaces on an atomic scale is now in progress with such tools as field emission microscopy, surface infrared and nuclear magnetic resonance spectroscopy, low-energy electron diffraction, electron-probe techniques, and surface conductance measurements. New insights into the nature and properties of surfaces become possible with the application of techniques such as ESCA,⁽¹²⁵⁾ secondary ion mass spectrometry,^(121,122,152) and ion scattering.⁽¹⁵³⁾ Further discussion of these methods will be found in Volume 6.

4. Utilization of Existing Techniques

4.1. Literature Examples

Published information on characterization of seven different materials has been gathered from the literature to serve as a guide to the use of existing analytical techniques. These seven materials are copper, silicon, gallium arsenide, potassium chloride, zinc sulfide, anthracene, and trace element glasses. Collectively they represent an extremely broad spectrum of analytical problems and illustrate both strong and weak points in the application of the present state of the art of measurement of composition.

The results, summarized in Tables 2–6, do not necessarily represent optimum performance, but they are fairly typical of published information on practical samples of highly purified materials. The notes of Tables 3–6 are quite representative of experience with different techniques on materials with impurities at levels of 500, 50, 1, or 0.02 ppm.

4.2. Factors Determining Use

These and other literature examples demonstrate the pronounced tendency of most investigators to use only a few, often only one, of the existing analytical techniques in characterization of materials. In the past the principal information on purity has been provided by emission spectroscopy, which was popular because it was broadly applicable and was a survey technique that required relatively small expense in terms of time, money, and sample size. Unfortunately, information at ppm levels derived by emission spectroscopy (see Table 2) is now often of marginal interest as impurity concentrations of 0.1–0.01 ppm and lower become important. The spark source mass spectrometer can now

TABLE 2
Published Data on Purified Materials

Materials	Method of preparation	Impurities (ppm)	Method of analysis
Copper ^(1,54)	Zone refined	Sb,* Cr(1), Co(60), Fe(10), Mn,* Ni(10), Si,* Ag,* Sn*	Emission spectroscopy
Copper ^(1,55)	Zone refined	Fe(0.5), As(<0.0001), Ag(0.01–0.02), Sb(<0.0001), Mn(<0.0001), Zn(<0.05), Na(<0.001), Cr(0.002–0.003), Ag(0.04), Se(<0.001), P(0.03–0.01)	Activation analysis
Silicon ^(1,56)	Thermal decomposition of silane	Fe(<0.017), Cu(0.011), Bi(<0.0016), As(0.0001), P(<0.001), Tl(<0.00091), Zn(<0.00041), Ni(<0.00027), In(<0.00032), Ga(<6.2 × 10 ⁻⁶), Sb(<3.7 × 10 ⁻⁶), Mn(<6.2 × 10 ⁻⁷)	Activation analysis
Silicon ^(1,57)	(Semiconductor material)	Fe, Ti, Bi, Pb, Zn, In, Cd, Ni, Cu (all at ~0.01 ppm)	Polarography
Gallium arsenide ^(1,34)	(Semiconductor material)	Si(0.03), Te(0.1)	Spectrophotometry
Gallium arsenide ^(2,3)	(Semiconductor material)	Stoichiometric within 0.007% (i.e., Ga/As = 1.000)	Coulometry
Potassium chloride ^(1,58)	Single-crystal growth from melt	Br(<1), C(<20), Fe(<1), I(<1), N(2), Na(<0.8) OH(0.01), P(<1), Pb(0.06), Rb(1), S(<1)	Spectroscopy, flame emission, atomic absorption, wet chemical, activation analysis

TABLE 2 (concluded)
Published Data on Purified Materials

Materials	Method of preparation	Impurities (ppm)	Method of analysis
Potassium chloride ^(1,5,9)	(Chemical reagent)	Bi, Pb, Ni, Cu, Fe, at 0.1 ppm level	Spectrophotometry
Zinc sulfide ^(1,6,1)	Single-crystal growth from vapor phase	Al(1.2), Ca (not detected), Cu(3), Fe(1.5), Mg(2), Mn(0.2), Ni(<1), Pb,* Sb(<10)	Emission spectroscopy
Anthracene ^(1,6,1)	Gas chromatography, zone refining, gradient sublimation, scavenging	Tetracene(<1), Anthraquinone(<1), Fluorene(<1), Phenanthrene(<1), Carbazole(1-10), Cr(<0.1), Fe(<0.5), Mg(<0.2), Pb(<0.1), Si(<0.5), Mn(<0.05), Cu(<0.1), Ag(<0.1), Al(<0.1)	Fluorescence, optical absorption, emission spectroscopy, gas chromatography
Trace element glasses ^(3,5)	Homogeneous batches of doped glass drawn into canes by modified Czochralski technique	(a) See Table 3 (b) See Table 4 (c) See Table 5 (d) See Table 6	Isotope dilution mass spectrometry, activation analysis, polarography, spectrophotometry, spark source mass spectrometry, flame emission, atomic absorption

* Not detected.

TABLE 3
Composition Values for NBS-SRM 610, 611⁽³⁵⁾; Trace Elements in a Glass Matrix, 500 ppm from Certificate of Analysis (Revised August 8, 1972)^a

Element	Value ^b	Notes ^c
Boron	(351)	1
Cobalt	(390)	2
Copper	(444 ± 4)	3
Gold	(25)	4
*Iron	458 ± 9	5
*Lead	426 ± 1	6
*Manganese	485 ± 10	7
*Nickel	458.7 ± 4	8
Potassium	(461)	1
*Rubidium	425.7 ± 0.8	9
Silver	(254 ± 10)	10
*Strontium	515.5 ± 0.5	11
Thallium	(61.8 ± 2.5)	12
*Thorium	457.2 ± 1.2	13
Titanium	(437)	14
*Uranium	461.5 ± 1.1	15
Zinc	(433)	16

^aThe present status of the analytical certification is given in the table. An asterisk before the element indicates a certified concentration for that element. The indicated limits on the concentration are equal to the entire range of observed results among sample points and/or the 95% confidence interval, whichever is larger. Values in parentheses are interim for the reasons given in the notes. Nominal composition of the support matrix is 72% SiO₂, 12% CaO, 14% Na₂O, and 2% Al₂O₃.

^bAll values given in table are in ppm by weight.

^cNotes: 1. Isotope dilution: interim value because of high blank. 2. Two independent sets of analyses by neutron activation disagree. 3. Isotope dilution: limits dictated by an observed trend in element concentration, well outside the precision of the method. 4. Spectrophotometry and neutron activation give grossly different results; value included only to indicate that the gold was not all lost in the processing of the glass rods. 5. Pooled value from data by spectrophotometry and polarography. 6. Pooled value from data by isotope dilution at two independent laboratories: NBS and USGS. 7. Value by spectrophotometry, substantiated by neutron activation. 8. Isotope dilution data accepted for certification, substantiated by spectrophotometry and polarography. 9. NBS isotope dilution data accepted for certification, cooperating analysts' data have a much larger uncertainty statement (range). 10. Isotope dilution: interim results because of questionable result on Rod No. 78 (8 ppm above average, not included in average). Neutron activation data have much larger range. 11. Pooled data: NBS isotope dilution data accepted and substantiated by USGS and Australian National University. The normalized ⁸⁷Sr/⁸⁶Sr ratio = 0.7094 ± 0.0002. 12. Isotope dilution: one method only, large uncertainty statement (range) is the result of a high value for Rod No. 2, which gave results 1.5 ppm higher than the average and was not included in the reported average. 13. Pooled isotope dilution data: NBS data accepted for certification and substantiated by USGS. 14. Polarographic: one method only. 15. Isotope dilution: NBS substantiated by USGS. Uranium in glass depleted in ²³⁵U. The atom per cent ²³⁵U = 0.2376. 16. Atomic absorption only: systematic error unknown.

TABLE 4
Composition Values for NBS-SRM 612, 613⁽³⁵⁾; Trace Elements in
Glass Matrix, 50 ppm from Certificate of Analysis (Revised August 8,
1972)^a

Element	Value ^b	Notes ^c
Barium	(41)	1
Boron	(32)	2
Cerium	(39)	1
Cobalt	(35.5 ± 1.2)	3
Copper	(37.7 ± 0.9)	4
Dysprosium	(35)	1
Erbium	(39)	1
Europium	(36)	1
Gadolinium	(39)	1
Gold	(5)	5
*Iron	51 ± 2	6
Lanthanum	(36)	1
*Lead	38.57 ± 0.2	7
Manganese	(39.6 ± 0.8)	8
Neodymium	(36)	1
*Nickel	38.8 ± 0.2	9
Potassium	(64)	10
*Rubidium	31.4 ± 0.4	11
Samarium	(39)	1
*Silver	22.0 ± 0.3	12
*Strontium	78.4 ± 0.2	13
Thallium	(15.7 ± 0.3)	4
*Thorium	37.79 ± 0.08	14
Titanium	(50.1 ± 0.8)	15
*Uranium	37.38 ± 0.08	16
Ytterbium	(42)	1

^a The present status of the analytical certification is given in the table. An asterisk before the element indicates a certified concentration for that element. The indicated limits on the concentration are equal to the entire range of observed results among sample points and/or the 95% confidence interval, whichever is larger. Values in parentheses are interim for the reasons given in the notes. Nominal composition of the support matrix is 72% SiO₂, 12% CaO, 14% Na₂O, and 2% Al₂O₃.

^b All values given in table are in ppm by weight.

^c Notes: 1. Isotope dilution: interim data from only two sample points. 2. Nuclear track counting plus two sample points by isotope dilution, insufficient precision and accuracy for certification. 3. Neutron activation: one method only. 4. Isotope dilution: one method only, observed range caused by sample variability. 5. Spectrophotometry and neutron activation give grossly different results; value included only to indicate that the gold was not all lost in the processing of the glass rods. 6. Pooled value from data by spectrophotometry and polarography. 7. Pooled isotope dilution data: NBS and USGS data weighed equally. 8. Spectrophotometry: one method only. 9. Isotope dilution data accepted for certification substantiated by spectrophotometry. 10. Interim data: isotope dilution and atomic absorption (both troubled with high blanks). 11. NBS isotope dilution data accepted for certification; cooperating analysts' data have a much larger uncertainty statement (range). 12. NBS isotope dilution data accepted for certification, substantiated by neutron activation. 13. Pooled data: NBS isotope dilution data accepted and substantiated by USGS and Australian National University. The normalized ⁸⁷Sr/⁸⁶Sr ratio = 0.7089 ± 0.0002. 14. Pooled isotope dilution data: NBS data accepted for certification and substantiated by USGS. 15. Polarographic: one method only. 16. Isotope dilution: NBS substantiated by USGS. Uranium in glass depleted in ²³⁵U. The atom per cent ²³⁵U = 0.2392.

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TABLE 5

Composition Values for NBS-SRM 614, 615⁽³⁵⁾; Trace Elements in a Glass Matrix, 1 ppm from Certificate of Analysis (Revised August 8, 1972)^a

Element	Value ^b	Notes ^c
Antimony	(1.06)	1
Boron	(1.30 ± 0.2)	2
Cadmium	(0.55)	3
Cobalt	(0.73 ± 0.02)	4
*Copper	1.37 ± 0.07	5
Europium	(0.99 ± 0.04)	4
Gallium	(1.3)	1
Gold	(0.5)	1
Iron	(13.3 ± 1)	6
Lanthanum	(0.83 ± 0.02)	4
*Lead	2.32 ± 0.04	7
Nickel	(0.95)	6
*Potassium	30 ± 1	8
*Rubidium	0.855 ± 0.005	9
Scandium	(0.59 ± 0.04)	4
*Silver	0.42 ± 0.04	10
*Strontium	45.8 ± 0.1	11
Thallium	(0.269 ± 0.005)	12
*Thorium	0.748 ± 0.006	13
Titanium	(3.1 ± 0.3)	6
*Uranium	0.823 ± 0.002	14

^a The present status of the analytical certification is given in the table. An asterisk before the element indicates a certified concentration for the element. The indicated limits on the concentration are equal to the entire range of observed results among sample points and/or the 95% confidence interval, whichever is larger. Values in parentheses are interim for the reasons given in the notes. Nominal composition of the support matrix is 72% SiO₂, 12% CaO, 14% Na₂O and 2% Al₂O₃.

^b All values given in the table are in ppm by weight.

^c Notes: 1. Neutron activation: one method only with an apparently large systematic error (> 10%) for this element because of poor correlation among measurements at various concentrations. 2. Nuclear track counting: one method only, but with very good correlation interpolating between concentrations. 3. Spark source isotope dilution: one method only. 4. Neutron activation: one method only. 5. Pooled data: spark source isotope dilution and the thermal ionization isotope dilution. 6. Polarographic: one method only. 7. Pooled isotope dilution data: value from USGS accepted because of smaller error limits and substantiated by NBS. 8. Pooled data: NBS flame emission data substantiated by NBS isotope dilution. 9. Isotope dilution data substantiated by flame emission which has a much larger uncertainty statement (range). 10. Pooled data: spark source isotope dilution plus neutron activation. 11. Pooled data: NBS isotope dilution data accepted and substantiated by USGS and Australian National University. The normalized ⁸⁷Sr/⁸⁶Sr ratio = 0.7083 ± 0.0002. 12. Isotope dilution: one method only with good correlation interpolating between concentrations. 13. Pooled isotope dilution data: value from NBS accepted because of smaller error limits and substantiated by USGS. 14. Isotope dilution: NBS isotope dilution data used, substantiated by USGS isotope dilution and NBS nuclear track counting data, which both had slightly higher uncertainties. Uranium in glass depleted in ²³⁵U. The atom per cent ²³⁵U = 0.2792.

TABLE 6
Composition Values for NBS-SRM 616, 617⁽³⁵⁾; Trace
Elements in a Glass Matrix, 0.02 ppm from Certificate
of Analysis (Revised August 8, 1972)^a

Element	Value ^b	Notes ^c
Antimony	(0.078 ± 0.007)	1
Boron	(0.20 ± 0.02)	2
Copper	(0.80 ± 0.09)	3
Gallium	(0.23 ± 0.02)	1
Gold	(0.18 ± 0.01)	1
Iron	(11 ± 2)	4
Lanthanum	(0.034 ± 0.007)	3
*Lead	1.85 ± 0.04	5
*Potassium	29 ± 1	6
Rubidium	(0.100 ± 0.007)	7
Scandium	(0.026 ± 0.012)	3
*Strontium	41.72 ± 0.05	8
Thallium	(0.0082 ± 0.0005)	9
*Thorium	0.0252 ± 0.0007	10
Titanium	(2.5 ± 0.7)	4
*Uranium	0.0721 ± 0.0013	11

^a The present status of the analytical certification is given in the table. An asterisk before the element indicates a certified concentration for that element. The indicated limits on the concentration are equal to the entire range of observed results among sample points and/or the 95% confidence interval, whichever is larger. Values in parentheses are interim for the reasons given in the notes. Nominal composition of the support matrix is 72% SiO₂, 12% CaO, 14% Na₂O and 2% Al₂O₃.

^b All values given in table are in ppm by weight.

^c Notes: 1. Neutron activation: one method only with an apparently large systematic error (> 10%) for this element because of poor correlation among measurements at various concentrations. 2. Nuclear track counting: one method only, but with very good correlation extrapolating down from 1 ppm glass. 3. Neutron activation: one method only with good correlation extrapolating down from 1 ppm glass. 4. Polarographic: one method only with good correlation extrapolating down from 1 ppm glass. The large uncertainty is due to a large chemical blank. 5. Pooled isotope dilution data: value from USGS accepted because of smaller error limits and substantiated by NBS. 6. Pooled data: NBS flame emission data substantiated by NBS isotope dilution. 7. Isotope dilution: one method only with good correlation extrapolating down from 1 ppm glass. The uncertainty statement (range) is the result of one sample point which gave a result 0.005 ppm higher than the average. 8. Pooled data: NBS isotope dilution data accepted and substantiated by NBS flame emission. The normalized ⁸⁷Sr/⁸⁶Sr ratio = 0.7080 ± 0.0002. 9. Isotope dilution: one method only with good correlation extrapolating down from 1 ppm glass. 10. Pooled isotope dilution data: value from NBS accepted because of smaller error limits and substantiated by USGS. 11. Pooled data: NBS and USGS isotope dilution data and NBS nuclear track counting all weighted equally. Uranium in glass depleted in ²³⁵U. The atom per cent ²³⁵U = 0.616.

TABLE 7
Current Use of Analytical Techniques

Technique	Use				Required for greater use			
	Low	Int.	High	Better training and education	More trained personnel	Greater convenience	Other	
Wet chemistry—gravimetry	—	—	×	—	—	—	Automation (with standards)	
Wet chemistry—titrimetry	—	—	×	—	—	—	Automation (with standards)	
Coulometry	×	—	—	×	×	—	Greater publicity	
Ion-selective electrodes	×	—	—	×	×	—	Development of interference-free procedures	
Polarography	—	×	—	×	×	—	—	
Spectrophotometry	—	—	×	—	—	—	—	
Spectrofluorimetry	×	—	—	—	×	—	Less sophisticated instrumentation	
Organic microanalysis	×	—	—	×	—	×	—	
Thin-layer chromatography	—	×	—	—	—	—	Improved means of quantitation	
Gas chromatography	—	—	×	—	—	—	Characterization of column materials for specific application	
Liquid chromatography	×	—	—	—	×	—	Choice of column conditions	
Neutron activation	—	×	—	—	×	×	Development of multielement approach	

TABLE 7 (continued)

Technique	Use			Required for greater use			
	Low	Int. High	High	Better training and education	More trained personnel	Greater convenience	Other
Vacuum fusion—Mass Spectrometry	—	×	—	—	×	×	—
Thermal analysis	—	×	—	×	—	—	Standards
X-ray fluorescence	—	—	×	—	—	—	Better standards
Spark source Mass spectrometry	—	×	—	—	—	×	More standards
Spark source mass spectrometry, Isotope dilution	×	—	—	×	—	—	—
Isotope dilution Mass spectrometry	×	—	—	×	—	—	General availability of better instrumentation
Emission spectroscopy	—	—	×	×	—	—	Better standards
Flame emission	—	×	—	×	—	—	Improvement in atomization; multielement approach
Atomic absorption	—	—	×	×	—	—	Improvement in atomization; multielement approach

TABLE 7 (concluded)

Technique	Use				Required for greater use			
	Low	Int.	High	Better training and education	More trained personnel	Greater convenience	Other	
Mössbauer spectroscopy	x	—	—	—	x	x	Application to more elements	
Nuclear magnetic resonance	—	x	—	—	x	—	—	
Electron spin resonance	x	—	—	—	x	—	—	
Residual resistance ratio	x	—	—	—	x	—	General availability of instrumentation	
Electron probe microanalysis	—	x	—	—	x	x	Automation	
Ion probe microanalysis	x	—	—	x	x	—	Development of lower cost instruments	
Photoelectron spectroscopy	x	—	—	x	x	—	General availability of better instrumentation	

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be expected to assume many of these survey functions to provide concentration information at the sub-ppm level.

There are only a modest number of research organizations with large analytical chemistry groups staffed with skilled professionals with the capability for comprehensive characterization of materials. Similarly, there are only a few analytical service laboratories capable of providing reliable composition values for materials research at a prescribed level of accuracy. The meaningful measurement of chemical composition is expensive. The materials investigator must plan to invest a significant portion of his resources in the determination of this "benchmark" analytical information that will enable him to reproduce his materials for future studies.

The availability of techniques, the availability of trained personnel, and the cost and time required for meaningful analytical measurements are all major factors in determining current utilization of existing analytical methods. Table 7 summarizes the best estimates on current use of these techniques.

Acknowledgments

The MAB Report that supplied the format and scientific approach for this chapter was the product of much thoughtful discussion among the members of the MAB Panel on Composition. Each panel member contributed to the original MAB Report in areas of his own expertise. Chairman Monroe Sadler edited these components into a final report that was reviewed by the panel for consistency and appropriateness.

For this chapter the original MAB Report contributions of the many NBS experts in specific analytical techniques have been revised and updated to represent the situation in January 1973. I would like to thank these many NBS contributors for their perceptive comments. The assistance of Mrs. Rosemary Maddock in the overall coordination of this manuscript, in particular in the preparation of the bibliography, is especially appreciated.

References

1. N. B. Hannay, Trace characterization and the properties of materials, in *Trace Characterization, Chemical and Physical* (W. W. Meinke and B. F. Scribner, eds.), pp. 5-38, NBS Monograph 100, U.S. Government Printing Office, Washington, D.C. (1967).

Characterization of Solids—Chemical Composition

2. R. A. Laudise, Opportunities for analytical chemistry in solid state research and electronics, in *Analytical Chemistry: Key to Progress on National Problems* (W. W. Meinke and J. K. Taylor, eds.), pp. 19–64, NBS Special Publication 351, U.S. Government Printing Office, Washington, D.C. (1972).
3. The Committee on Characterization of Materials, Materials Advisory Board, Division of Engineering, National Research Council, National Academy of Sciences, National Academy of Engineering, *Characterization of Materials*, MAB-229-M, U.S. Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia (1967).
4. G. E. F. Lundell, The chemical analysis of things as they are, *Ind. and Eng. Chem. (Anal. Ed.)* **5**, 221–225 (1933).
5. P. Albert, A combination of chemical and physiochemical methods for a systematic separation of large numbers of radioisotopes on one experimental analysis of aluminum, iron, and zirconium by radioactivation, in *Modern Trends in Activation Analysis* (Proc. 1961 Int. Conf. on Modern Trends in Activation Analysis, College Station, Texas, December 1961), pp. 86–94, Texas A & M University, College Station, Texas (1962).
6. I. M. Kolthoff and P. J. Elving (eds.), *Treatise on Analytical Chemistry, A Comprehensive Account in three parts, Part I: Theory and Practice* (10 vols.), *Part II: Analytical Chemistry of the Elements* (14 vols.), *Part III: Analysis of Industrial Products* (2 vols.), Interscience, New York (1959–1971).
7. W. W. Meinke and B. F. Scribner (eds.), *Trace Characterization, Chemical and Physical* (Proc. 1st Materials Research Symp., October 1966), NBS Monograph 100, U. S. Government Printing Office, Washington, D.C. 20402 (1967).
8. Analytical reviews 1972, Fundamentals, *Anal. Chem.* **44**(5), 1R-572R (1972).
9. Analytical reviews 1971, Applications, *Anal. Chem.* **43**(5), 1R-388R (1971).
10. W. W. Meinke, Is radiochemistry the ultimate in trace analysis?, Proc. Int. Conf. on Analytical Chemistry, Kyoto, Japan, April 1972, *Pure and Appl. Chem.* **34**, 93–104 (1973).
11. W. W. Meinke, The ultimate contribution of nuclear activation analysis, Proc. of 4th Int. Conf. on Modern Trends in Activation Analysis, Saclay, France, October 1972, *J. Radioanalytical Chem.* (in press).
12. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, *Applied Inorganic Analysis*, 2nd ed., Wiley, New York (1953).
13. I. M. Kolthoff and P. J. Elving (eds.), *Treatise on Analytical Chemistry*, Part 1, Vol. 1; Part 2, Vols. 1–14, Wiley—Interscience, New York (1959–1971).
14. L. Erdey, L. Pólos, and R. A. Chalmers, Development and publication of new gravimetric methods of analysis, *Talanta* **17**, 1143–1155 (1970).
15. E. B. Sandell, Errors in chemical analysis, in *Treatise on Analytical Chemistry* (I. M. Kolthoff and P. J. Elving, eds.), Part 1, Vol. 1, pp. 19–46, The Interscience Encyclopedia, Inc., New York (1959).
16. A. Ringbom, *Complexation in Analytical Chemistry*, Interscience, New York (1963).
17. J. R. Bacon and R. B. Ferguson, Gravimetric and coulometric analysis of beryllium samples using 2-methyl-8-quinolinol, *Anal. Chem.* **44**, 2149–2152 (1972).
18. R. S. Danchik, Analytical reviews 1971/Applications: Nonferrous metallurgy. 1. Light metals: aluminum, beryllium, titanium, and magnesium, *Anal. Chem.* **43**(5), 109R–145R (1971).

Chapter 7

19. R. P. Buck, Analytical reviews 1972/Fundamentals: Ion-selective electrodes, potentiometry, and potentiometric titrations, *Anal. Chem.* **44**(5), 270R–295R (1972).
20. G. Marinenko and C. E. Champion, High-precision coulometric titrations of boric acid, *J. Res. NBS (U.S.)*, **75A (Phys. and Chem.)**, 421–428 (1971).
21. C. E. Champion, G. Marinenko, J. K. Taylor, and W. E. Schmidt, Determination of submicrogram amounts of chromium by coulometric titrimetry, *Anal. Chem.* **42**, 1210–1213 (1970).
22. G. Marinenko and J. K. Taylor, High-precision coulometric iodimetry, *Anal. Chem.* **39**, 1568–1571 (1967).
23. G. Marinenko, Gallium arsenide stoichiometry, in *Electrochemical Analysis Section, Summary of Activities, July 1970 to June 1971* (R. A. Durst, ed.), pp. 24–29, NBS Technical Note 583, U. S. Government Printing Office, Washington, D.C. (1973).
24. G. Marinenko and J. K. Taylor, Electrochemical equivalents of benzoic and oxalic acid, *Anal. Chem.* **40**, 1645–1651 (1968).
25. G. Marinenko and R. T. Foley, A new determination of the atomic weight of zinc, *J. Res. NBS (U.S.)*, **75A (Phys. and Chem.)**, 561–564 (1971).
26. K. M. Sappenfield, G. Marinenko, and J. L. Hague, *Standard Reference Materials: Comparison of Redox Standards*, NBS Special Publication 260-24, U.S. Government Printing Office, Washington, D. C. (1972).
27. R. A. Durst (ed.), *Ion-Selective Electrodes* (Proc. of a Symp. on Ion-Selective Electrodes, January 1969), NBS Special Publications 314, U.S. Government Printing Office, Washington, D.C. (1969).
28. J. Koryta, Theory and applications of ion-selective electrodes, *Anal. Chim. Acta* **61**, 329–411 (1972).
29. R. A. Durst, Ion-selective electrodes in science, medicine, and technology, *Am. Scientist* **59**, 353–361 (1971).
30. L. Meites, *Polarographic Techniques*, 2nd ed., Interscience, New York (1965).
31. D. D. Gilbert, Electroanalytical methods, in *Guide to Modern Methods of Instrumental Analysis* (T. H. Gouw, ed.), pp. 393–431, Wiley—Interscience, New York (1972).
32. E. J. Maienthal, Polarographic analysis at NBS, *Am. Laboratory* **4**(6), 12–21 (1972).
33. T. M. Florence, Anodic stripping voltammetry with a glassy carbon electrode mercury-plated *in situ*, *J. Electroanal. Chem.* **27**, 273–281 (1970).
34. E. J. Maienthal and J. K. Taylor, Improvement of polarographic precision by a comparative technique, *Mikrochim. Acta* **1967**, 939–945.
35. Certificates of analysis (provisional): Trace elements in a glass matrix, standard reference materials 610 and 611 (trace element concentration 500 ppm); 612 and 613 (trace element concentration 50 ppm); 614 and 615 (trace element concentration 1 ppm); and 616 and 617 (trace element concentration 0.02 ppm); August 5, 1970, revised August 8, 1972; available from Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C.
36. I. L. Barnes, B. S. Carpenter, E. L. Garner, J. W. Gramlich, E. C. Kuehner, L. A. Machlan, E. J. Maienthal, J. R. Moody, L. J. Moore, T. J. Murphy, P. J. Paulsen, K. M. Sappenfield, and W. R. Shields, Isotopic abundance ratios and concentra-

Characterization of Solids—Chemical Composition

- tions of selected elements in Apollo 14 samples, *Proc. Third Lunar Science Conf., Geochim. Cosmochim. Acta*, Supplement 3, Vol. 2, pp. 1465–1472, MIT Press, Cambridge, Mass. (1972).
37. E. J. Maienthal, Analysis of botanical standard reference materials by cathode ray polarography, *J. Assoc. Official Analytical Chemists* **55**, 1109–1113 (1972).
 38. T. S. West, Chemical spectrophotometry in trace characterization, in *Trace Characterization, Chemical and Physical* (W. W. Meinke and B. F. Scribner, eds.), pp. 215–301, NBS Monograph 100, U.S. Government Printing Office, Washington, D.C. (1967).
 39. J. D. Ingle, Jr. and S. R. Crouch, Pulse overlap effects on linearity and signal-to-noise ratio in photon counting systems, *Anal. Chem.* **44**, 777–783 (1972).
 40. S. Shibata, M. Furukawa, and K. Goto, Dual-wavelength spectrophotometry. Part II. The determination of mixtures, *Anal. Chim. Acta* **53**, 369–377 (1971).
 41. T. J. Porro, Double-wavelength spectroscopy, *Anal. Chem.* **44**(4), 93A–103A (1972).
 42. D. M. Dodd, D. L. Wood, and R. L. Barns, Spectrophotometric determination of chromium concentration in ruby, *J. Appl. Phys.* **35**, 1183–1186 (1964).
 43. C. E. White and R. J. Argauer, *Fluorescence Analysis*, Marcel Dekker, New York (1970).
 44. R. Mavrodineanu, J. I. Shultz, and O. Menis (eds.), Accuracy in spectrophotometry and luminescence measurements, Part 2. Luminescence, Proc. Conf. on Accuracy in Spectrophotometry and Luminescence Measurements, March 1972, *J. Res. NBS (U.S.)*, **76A (Phys. and Chem.)**, 547–654 (1973); also NBS Special Publication 378, U. S. Government Printing Office, Washington, D.C. (1973).
 45. C. A. Parker, Spectrophosphorimeter microscopy: an extension of fluorescence microscopy, *The Analyst* **94**, 161–176 (1969).
 46. S. Udenfriend, *Fluorescence Assay in Biology and Medicine*, Vols. I, II, Academic, New York (1962, 1969).
 47. J. P. Dixon, *Modern Methods of Organic Microanalysis*, Van Nostrand, Princeton, New Jersey (1968).
 48. G. Tölg, *Ultramicro Elemental Analysis*, Wiley-Interscience New York (1970).
 49. H. Weisz, *Microanalysis by the Ring-Oven Technique*, 2nd ed., Pergamon, New York (1970).
 50. F. Feigl, *Spot Tests in Organic Analysis*, 7th ed., Elsevier, Amsterdam (1966).
 51. E. Stahl, *Thin-Layer Chromatography*, Springer-Verlag, New York (1969).
 52. A. Niederwieser and G. Pataki (eds.), *Progress in Thin-Layer Chromatography and Related Methods*, Vol. I (1970), Vol. II (1970), Vol. III (1972), Ann Arbor-Humphrey Science Publishers, Ann Arbor.
 53. S. Dal Nogare and R. S. Juvet, Jr., *Gas—Liquid Chromatography, Theory and Practice*, Interscience, New York (1962).
 54. A. E. Pierce, *Silylation of Organic Compounds*, Pierce Chemical Co., Rockford, Illinois (1968).
 55. R. W. McKinney, Pyrolysis gas chromatography, in *Ancillary Techniques of Gas Chromatography* (L. S. Ettre and W. H. McFadden, eds.), pp. 55–87, Wiley-Interscience, New York (1969).
 56. M. Beroza and M. N. Inscoe, Precolumn reactions for structure determination, in *Ancillary Techniques of Gas Chromatography* (L. S. Ettre and W. H. McFadden, eds.), pp. 89–144, Wiley-Interscience, New York (1969).

Chapter 7

57. A. J. Raymond, D. M. G. Lawrey, and T. J. Mayer, Acquisition and processing of gas chromatographic data using a time-shared computer, *J. Chromatog. Sci.* **8**, 1–12 (1970).
58. J. J. Kirkland, *Modern Practice of Liquid Chromatography*, Wiley–Interscience, New York (1971).
59. J. J. Kirkland, Columns for modern analytical liquid chromatography, *Anal. Chem.* **43**(12), 36A–48A (1971).
60. H. Veening, Liquid chromatography detectors, *J. Chem. Ed.* **47**, A549–A568, A675–A686, A749–A762 (1970).
61. P. Kruger, *Principles of Activation Analysis*, Wiley–Interscience, New York (1971).
62. J. R. DeVoe and P. D. LaFleur (eds.), *Modern Trends in Activation Analysis* (Proc. 1968 Int. Conf. on Modern Trends in Activation Analysis, October 1968), NBS Special Publication 312, Vols. I and II, U.S. Government Printing Office, Washington, D.C. (1969).
63. G. J. Lutz, R. J. Boreni, R. S. Maddock, and J. Wing (eds.), *Activation Analysis: A Bibliography Through 1971*, NBS Technical Note 467, U.S. Government Printing Office, Washington, D.C. (1972).
64. D. DeSoete, R. Gijbels, and J. Hoste, *Neutron Activation Analysis*, Wiley, New York (1972).
65. G. J. Lutz, Photon activation analysis—a review, *Anal. Chem.* **43**, 93–103 (1971).
66. E. A. Schweikert and H. L. Rook, Determination of oxygen in silicon in the sub-part-per-million range by charged-particle activation analysis, *Anal. Chem.* **42**, 1525–1527 (1970).
67. W. S. Horton and C. C. Carson, Gas analysis: Determination of gases in metals, in *Treatise on Analytical Chemistry* (I. M. Kolthoff and P. J. Elving, eds.), Part I, Vol. 10, Section E, Chapter 103, pp. 6017–6144, Wiley, New York (1972).
68. O. Menis and J. T. Sterling, *Standard Reference Materials: Determination of Oxygen in Ferrous Metals—SRM 1090, 1091 and 1092*, National Bureau of Standards Misc. Publ. 260-14, U.S. Government Printing Office, Washington, D.C. (1966).
69. K. W. Guardipee, Two methods for separation of surface and bulk gases in vacuum-fusion analysis of metals, *Anal. Chem.* **42**, 469–473 (1970).
70. J. W. Frazer, Digital control computers in analytical chemistry, *Anal. Chem.* **40**(8), 26A–40A (1968).
71. P. D. Garn, *Thermoanalytical Methods of Investigation*, Academic, New York (1965).
72. R. F. Schwenker, Jr. and P. D. Garn (eds.), *Thermal Analysis*, Vol. 1, *Instrumentation, Organic Materials, and Polymers*, Vol. 2, *Inorganic Materials and Physical Chemistry*, Academic, New York (1969).
73. O. Menis (ed.), *Status of Thermal Analysis* (Proc. Symp. on the Current Status of Thermal Analysis, April 1970), NBS Special Publication 338, U.S. Government Printing Office, Washington, D.C. (1970).
74. H. G. Wiedemann (ed.), *Thermal Analysis*, Vol. 1, *Advances in Instrumentation*, Vol. 2, *Inorganic Chemistry*, Vol. 3, *Organic and Macromolecular Chemistry, Ceramics, Earth Science*, Birkhäuser, Basel, Switzerland (1972).
75. C. B. Murphy, Analytical reviews 1972/Fundamentals: Thermal analysis, *Anal. Chem.* **44**(5), 513R–524R (1972).

Characterization of Solids—Chemical Composition

76. 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).
77. R. O. Müller, *Spectrochemical Analysis by X-Ray Fluorescence* (K. Keil, transl.), Plenum, New York (1972).
78. C. L. Luke, Determination of trace elements in inorganic and organic materials by x-ray fluorescence spectroscopy, *Anal. Chim. Acta* **41**, 237–250 (1968).
79. L. S. Birks, Analytical reviews 1972/Fundamentals: X-ray absorption and emission, *Anal. Chem.* **44**(5), 557R–562R (1972).
80. R. D. Giauque and J. M. Jaklevic, Rapid quantitative analysis by x-ray spectrometry, in *Advances in X-ray Analysis* (K. F. J. Heinrich, C. S. Barrett, J. B. Newkirk, and C. O. Ruud, eds.), Vol. 15, pp. 164–175, Plenum, New York (1972).
81. R. Brown, M. L. Jacobs, and H. E. Taylor, A survey of the most recent applications of spark source mass spectrometry, *Am. Laboratory* **4**(11), 29–40 (1972).
82. R. A. Bingham and R. M. Elliott, Accuracy of analysis by electrical detection in spark source mass spectrometry, *Anal. Chem.* **43**, 43–54 (1971).
83. P. J. Paulsen, R. Alvarez, and C. W. Mueller, Spark source mass spectrographic analysis of ingot iron for Ag, Cu, Mo, and Ni by isotope dilution and for Co by an internal standard technique, *Anal. Chem.* **42**, 673–675 (1970).
84. E. C. Kuehner, R. Alvarez, P. J. Paulsen, and T. J. Murphy, Production and analysis of special high-purity acids purified by sub-boiling distillation, *Anal. Chem.* **44**, 2050–2056 (1972).
85. C. C. McMullen and H. G. Thode, Isotope abundance measurements and their application to chemistry, in *Mass Spectrometry* (A. McDowell, ed.), pp. 375–441, McGraw-Hill, New York (1963).
86. I. L. Barnes, E. L. Garner, J. W. Gramlich, L. J. Moore, T. J. Murphy, L. A. Machlan, W. R. Shields, M. Tatsumoto, and R. J. Knight, The determination of lead, uranium, thorium and thallium in silicate glass standard materials, *Anal. Chem.* **45**, 880–885 (1973).
87. Certificates of analysis (provisional): Orchard leaves, standard reference material 1571 (October 1, 1971); Bovine liver, Standard Reference material 1577 (April 15, 1972); available from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C.
88. B. F. Scribner and M. Margoshes, Emission spectroscopy, in *Treatise on Analytical Chemistry* (I. M. Kolthoff and P. J. Elving, eds.), Part I, Vol. 6, Chapter 64, pp. 3347–3461, Interscience, New York (1965).
89. E. L. Grove (ed.), *Analytical Emission Spectroscopy*, Vol. I, Part I (Analytical Spectroscopy Series, Vol. II, 1972; Vol. III, to be published), Marcel Dekker, New York (1971).
90. V. G. Mossotti, Emission spectroscopy including dc arc, spark, and other methods, in *Techniques of Metals Research* (R. F. Bunshah, ed.), Vol. III, Part 2, pp. 533–572, Interscience, New York (1970).
91. R. M. Barnes, Analytical reviews 1972/Fundamentals: Emission spectrometry, *Anal. Chem.* **44**(5), 122R–150R (1972).
92. J. A. Dean and T. C. Rains, *Flame Emission and Atomic Absorption Spectrometry*, Vol. 1, *Theory*, Vol. 2, *Components and Techniques*, Marcel Dekker, New York (1969, 1971).

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93. R. Mavrodineanu (ed.), *Analytical Flame Spectroscopy, Selected Topics*, Macmillan, London (1970).
94. E. E. Pickett and S. R. Koirtyohann, Emission flame photometry—A new look at an old method, *Anal. Chem.* **41**(14), 28A–42A (1969).
95. D. P. Hubbard, *Annual Reports on Analytical Atomic Spectroscopy 1971*, Vol. 1, The Society for Analytical Chemistry, London (1972).
96. G. D. Christian and F. J. Feldman, A comparison study of detection limits using flame-emission spectroscopy with the nitrous oxide—acetylene flame and atomic-absorption spectroscopy, *Appl. Spectr.* **25**, 660–663 (1971).
97. J. W. Robinson and P. J. Slevin, Recent advances in instrumentation in atomic absorption, *Am. Laboratory* **4**(8), 10–18 (1972).
98. G. F. Kirkbright, The application of non-flame atom cells in atom-absorption and atomic-fluorescence spectroscopy, a review, *The Analyst* **96**, 609–623 (1971).
99. V. I. Goldanskii and R. H. Herber, *Chemical Applications of Mössbauer Spectroscopy*, Academic, New York (1968).
100. L. May, *An Introduction to Mössbauer Spectroscopy*, Plenum, New York (1971).
101. G. Stevens, J. C. Travis, and J. R. DeVoe, Analytical reviews 1972/Fundamentals: Mössbauer spectrometry, *Anal. Chem.* **44**(5), 384R–406R (1972).
102. R. L. Mössbauer, Gamma resonance spectroscopy and chemical bonding, *Angew. Chem. Internat. Ed.* **10**, 462–472 (1971).
103. J. J. Spijkerman and P. A. Pella, A review of selected highlights of Mössbauer spectrometry, *Crit. Rev. Anal. Chem.* **1**, 7–45 (1970).
104. R. M. Lynden-Bell and R. K. Harris, *Nuclear Magnetic Resonance Spectroscopy*, Nelson, London (1969).
105. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Vols. 1, 2, Pergamon, New York (1965, 1966).
106. F. A. Bovey, *Nuclear Magnetic Resonance Spectroscopy*, Academic, New York (1969).
107. C. A. Poole, Jr. and H. A. Farach, *Relaxation in Magnetic Resonance; Dielectric and Mössbauer Applications*, Academic, New York (1971).
108. J. I. Kaplan, Numerical solution of the equation governing nuclear magnetic spin–lattice relaxation in a paramagnetic-spin-doped insulator, *Phys. Rev.* **B3**, 604–607 (1971).
109. J. E. Wertz and J. R. Bolton, *Electron Spin Resonance: Elementary Theory and Practical Applications*, McGraw-Hill, New York (1972).
110. F. Gerson, *High Resolution Electron Spin Resonance Spectroscopy*, Wiley, New York (1970).
111. A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Oxford, Clarendon Press, London (1970).
112. L. R. Weisberg, Electrical measurement for trace characterization, in *Trace Characterization, Chemical and Physical* (W. W. Meinke and B. F. Scribner, eds.), NBS Monograph 100, U.S. Government Printing Office, Washington, D.C. (1967).
113. V. A. Deason, A. F. Clark, and R. L. Powell, Characterization of high purity metals by the residual resistivity ratio, *Mat. Res. and Std.* **1971**(8), 25–28.
114. A. F. Clark, V. A. Deason, J. G. Hust, and R. L. Powell, *Standard Reference Materials: The Eddy Current Decay Method for Resistivity Characterization of High Purity Metals*, NBS Special Publication 260-39, U.S. Government Printing Office, Washington, D.C. (1972).

Characterization of Solids—Chemical Composition

115. L. S. Birks, *Electron Probe Microanalysis*, 2nd ed., Wiley—Interscience, New York (1971).
116. K. F. J. Heinrich, *Scanning electron probe microanalysis*, NBS Technical Note 278, U.S. National Technical Information Service, Springfield, Virginia (1967).
117. K. F. J. Heinrich, *Quantitative Electron Probe Microanalysis*, NBS Special Publication 298, U.S. Government Printing Office, Washington, D.C. (1968).
118. K. F. J. Heinrich, Errors in theoretical correction systems in quantitative electron probe microanalysis—A synopsis, *Anal. Chem.* **44**, 350–354 (1972).
119. R. Tixier and J. Philibert, Analyse quantitative d'échantillons minces, in *Proc. 5th Int. Congress on X-Ray Optics and Microanalysis* (G. Möllenstedt and K. H. Gaukler, eds.), pp. 180–186, Springer-Verlag, Berlin (1968).
120. W. J. Campbell and J. V. Gilfrich, Analytical reviews 1970/Fundamentals: X-ray absorption and emission, *Anal. Chem.* **42**(5), 248R–268R (1970).
121. A. J. Socha, Analysis of surfaces utilizing sputter ion source instruments, *Surface Sci.* **25**, 147–170 (1971).
122. A. Benninghoven, Beobachtung von Oberflächenreaktionen mit der statischen Methode der Sekundärionen-massenspektroskopie; I. Die Methode, *Surface Sci.* **28**, 541–562 (1971); A. Benninghoven, Surface investigation of solids by the statistical method of secondary ion mass spectroscopy (SIMS) *Surface Sci.* **35**, 427–457 (1973).
123. C. A. Anderson, Progress in analytical methods for the ion microprobe mass analyzer, *Int. J. Mass Spectry. Ion Phys.* **2**, 61–74 (1969).
124. J. A. McHugh and J. F. Stevens, Elemental analysis of single micrometer-size airborne particulates by ion microprobe mass spectrometry, *Anal. Chem.* **44**, 2187–2192 (1972).
125. K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. Karlsson, I. Lindgren, and B. Lindberg, *ESCA: Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy*, Nova Acta Regiae Societatis Scientiarum Upsaliensis, Series IV, Vol. 20, Almqvist and Wiksells Boktryckeri AB Uppsala (1967).
126. D. A. Shirley (ed.), *Electron Spectroscopy*, North-Holland, Amsterdam (1972).
127. D. M. Hercules, Analytical reviews 1972/Fundamentals: Electron spectroscopy. II, X-ray photoexcitation, *Anal. Chem.* **44**(5), 106R–112R (1972).
128. K. Siegbahn, D. Hammond, H. Fellner-Feldegg, and E. F. Barnett, Electron spectroscopy with monochromatized x-rays, *Science* **176**, 245–252 (1972).
129. W. H. McCurdy, Jr. and D. H. Wilkins, Analytical reviews 1966/Fundamentals: Volumetric and gravimetric analytical methods for inorganic compounds, *Anal. Chem.* **38**, 469R–478R (1966).
130. A. L. Underwood, Photometric titration, in *Advances in Analytical Chemistry and Instrumentation* (C. N. Reilley, ed.), Vol. 3, pp. 31–104, Interscience, New York (1964).
131. G. Marinenko and J. K. Taylor, Precise coulometric titration of dichromate, *J. Res. NBS (U.S.)*, **76A** (*Phys. and Chem.*), 453–459 (1963).
132. T. M. Florence, Ion-selective electrodes, *Proc. Roy. Austral. Chem. Inst.* **37**, 261–270 (1970).
133. T. S. West, Some sensitive and selective reactions in inorganic spectroscopic analysis, *The Analyst* **91**, 69–77 (1966).

Chapter 7

134. J. A. Roberts, J. Winwood, and E. J. Millett, The spectrophotometric determination of sub-microgram amounts of impurities in semiconductor materials, in *Proc. Soc. Analytical Chemistry Conf., Nottingham, 1965*, pp. 528–538, Heffer & Sons, Cambridge (1965).
135. I. P. Alimarin, Progress and problems of trace determination in pure substances, *Zh. Analit. Khim.* **18**, 1412–1425 (1963).
136. M. Vecera and J. Horska, A study of the accuracy and precision of methods for the determination of carbon and hydrogen in organic compounds, *Pure Appl. Chem.* **21**(1), 47–84 (1970).
137. N. Hadden, F. Baumann, F. MacDonald, M. Munc, R. Stevenson, D. Gere, F. Zamaroni, and R. Majors, *Basic Liquid Chromatography*, Varian Aerograph, Walnut Creek, California (1971).
138. J. M. A. Lenihan and S. J. Thomson (eds.), *Advances in Activation Analysis*, Vol. 2, Academic, New York (1972).
139. J. P. Bruch, Determination of gases in steel and application of the results, Iron and Steel Institute Special Report No. 131, *Determination of Chemical Composition—Its Application and Process Control*, Iron and Steel Institute, London (1971).
140. W. Schwarz and H. Zitter, Determination for oxygen content in steel by hot extraction, *Berg. Hutten. Monatsh.* **113**, 1–10 (1968).
141. C. Mazieres, Differential thermal microanalysis, physical chemical applications, *Bull. Soc. Chim. France* **1961**, 1695–1701.
142. G. V. Davis and R. S. Porter, Application of the differential scanning calorimeter to purity measurements, *J. Thermal Anal.* **1**, 449–458 (1969).
143. N. W. H. Addink, *DC Arc Analysis*, Macmillan, London (1971).
144. M. D. Amos, P. A. Bennett, K. G. Brodie, P. W. Y. Lung, and J. P. Matousek, Carbon rod atomizer in atomic absorption and fluorescence spectrometry and its clinical application, *Anal. Chem.* **43**, 211–215 (1971).
145. P. A. Pella and J. R. DeVoe, Determination of tin in copper-base alloys by Mössbauer spectroscopy, *Anal. Chem.* **42**, 1833–1835 (1970).
146. L. H. Schwartz, Quantitative analysis using Mössbauer effect spectroscopy, *Int. J. Nondestruct. Test.* **1**, 353–381 (1970).
147. P. A. Pella and J. R. DeVoe, International standardization in Mössbauer spectrometry, *Appl. Spectry.* **25**, 472–474 (1971).
148. T. C. Farrar and E. D. Becker, *Pulse and Fourier Transform NMR*, Academic, New York (1971).
149. R. S. Alger, *Electron Paramagnetic Resonance: Techniques and Applications*, Section 3.3, Sensitivity, pp. 69–91, Interscience, New York (1968).
150. C. P. Poole, Jr., *Electron Spin Resonance: A Comprehensive Treatise on Experimental Techniques*, pp. 523–600, Interscience, New York (1967).
151. R. F. Gould, *Nonstoichiometric Compounds*, Advances in Chemistry Series 39, American Chemical Society, Washington, D.C. (1963).
152. A. Benninghoven, Mass spectrometric analysis of monomolecular layers of solids by secondary ion emission, in *Advances in Mass Spectrometry* (A. Quale, ed.), Vol. 5, pp. 444–447, Elsevier, New York (1971).
153. D. P. Smith, Analysis of surface composition with low-energy backscattered ions, *Surface Sci.* **25**, 171–191 (1971).
154. E. D. Tolmie and D. A. Robins, The zone-refining of impure copper, *J. Inst. Metals* **85**, 171–176 (1957).

Characterization of Solids—Chemical Composition

155. M. Cuypers, Systematic analysis of high purity copper, following its irradiation by thermal neutrons, *Ann. Chim. (Paris)* **9**, 509–540 (1964).
156. C. H. Lewis, M. B. Giusto, H. C. Kelly, and S. Johnson, The preparation of high-purity silicon from silane, in *Ultrapurification of Semiconductor Materials* (M. S. Brooks and J. K. Kennedy, eds.), pp. 55–56, Macmillan, New York (1962).
157. F. A. Pohl and W. Bonsels, Zur spurenanalyse sehr reinen siliciums, *Mikrochim. Acta* **1960**, 641–649.
158. C. T. Butler, J. R. Russell, R. B. Quincy, Jr., and D. E. LaValle, A method for purification and growth of KCl single crystal, Oak Ridge National Laboratory Technical Report ORNL-3906, U.S. Atomic Energy Commission Technical Information Center, Oak Ridge, Tennessee.
159. A. Glasner and P. Avinur, Spectrophotometric methods for the determination of impurities in pure and analytical reagents—III. The determination of six ions in KCl, *Talanta* **11**, 775–780 (1964).
160. A. Kremheller, Growth and heat treatment of zinc sulfide single crystals, *J. Electrochem. Soc.* **107**, 422–427 (1960).
161. G. J. Sloan, Studies on the purification of anthracene; determination and use of segregation coefficients, *Molecular Crystals* **1**, 161–194 (1966).