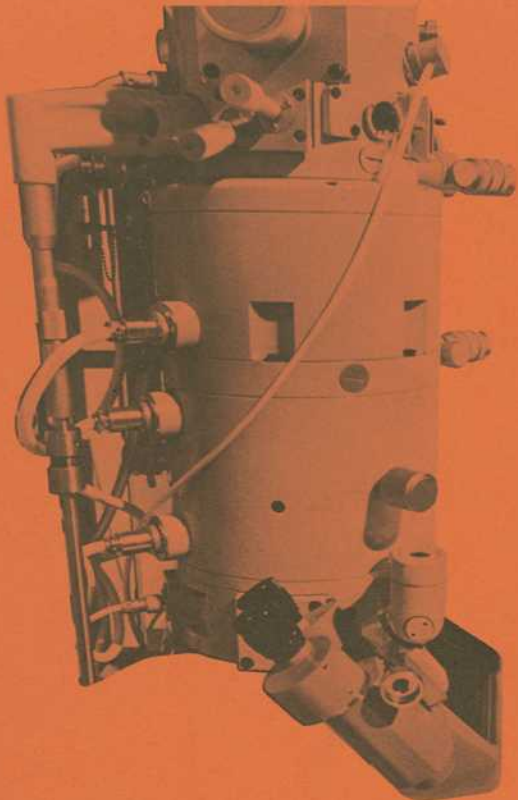




ELECTRON BEAM MICROANALYSIS

D. R. Beaman
and
J. A. Isasi

STP 506



AMERICAN SOCIETY FOR TESTING AND MATERIALS

Electron Beam Microanalysis

by **D. R. Beaman and J. A. Isasi**

ASTM SPECIAL TECHNICAL PUBLICATION 506

**List price: \$3.75
04-506000-28**



AMERICAN SOCIETY FOR TESTING AND MATERIALS

1916 Race Street, Philadelphia, Pa. 19103

© by the American Society for Testing and Materials 1972
Library of Congress Catalog Number: 74-189005

(Second Printing, January 1974)

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Printed in Baltimore, Md.

Foreword

In recent years the development of new scientific instruments and techniques has made microanalysis an essential and powerful tool for the materials scientist. The ability to chemically characterize small, included particles or second-phase materials down to one micrometer ($1\text{ }\mu\text{m}$) in diameter and to determine the nature of surfaces with a depth resolution below $100\text{\AA}$ has led to the solution of serious materials problems and the development of new products and processes. This article, which is a review of the many techniques available, illustrates how the various techniques are related, when they can be most appropriately used and when they can be successfully combined in a single instrument. Such a review should: 1) aid the materials scientist in selecting the proper technique and instrument for his particular problem; 2) guide the novice in his initial efforts in the field of microanalysis; and 3) provide the expert with a critical review and state-of-the-art description of the field. Particular emphasis is placed on the quantitative capabilities of the various techniques so that the reader may obtain a full understanding of the capabilities and limitations of each. The problems associated with accuracy and precision in electron beam microanalysis are discussed so the investigator or user will be aware of potential problems. The following instruments and techniques or combinations thereof are discussed: electron probe analyzer, transmission electron microscope, scanning electron microscope, Auger electron spectroscopy, energy dispersive spectrometer, ion mass analyzer, automated instruments and quantitative metallography. Finally applications in many disciplines are presented to illustrate the vast potential of the techniques.

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Part I—The Fundamentals and Applications

Electron Beam Microanalysis

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Introduction

The Proven Usefulness of Chemical Microanalysis/ The electron probe analyzer is a scientific instrument that, in a short period of time, has been successfully and widely used in many scientific disciplines and has contributed in a significant manner to improved living conditions and to the reservoir of scientific knowledge. These benefits have accrued, despite its high initial cost and the high degree of competence required to operate, maintain, and fully understand the instrument and its capabilities, from the ability of the instrument to chemically analyze extremely small volumes of material, such as the nucleus of an individual white blood cell or a particle in a precipitation hardened material.

The electron probe analyzer, or EPA (not to be confused with the newly created Environmental Protection Agency), of which there are over 400 in the United States and over 700 worldwide, is used in research, development, and quality control in such diverse scientific areas as metallurgy, mineralogy, criminology, biochemistry, pathology, zoology, agronomy, physics, and electronics. While the instrument has made its greatest impact in the study of materials and minerals, its use in other areas is rapidly expanding and the technique holds particular promise in the areas of biology and environmental science. By way of example, in our own laboratories, during the last three years, we have analyzed

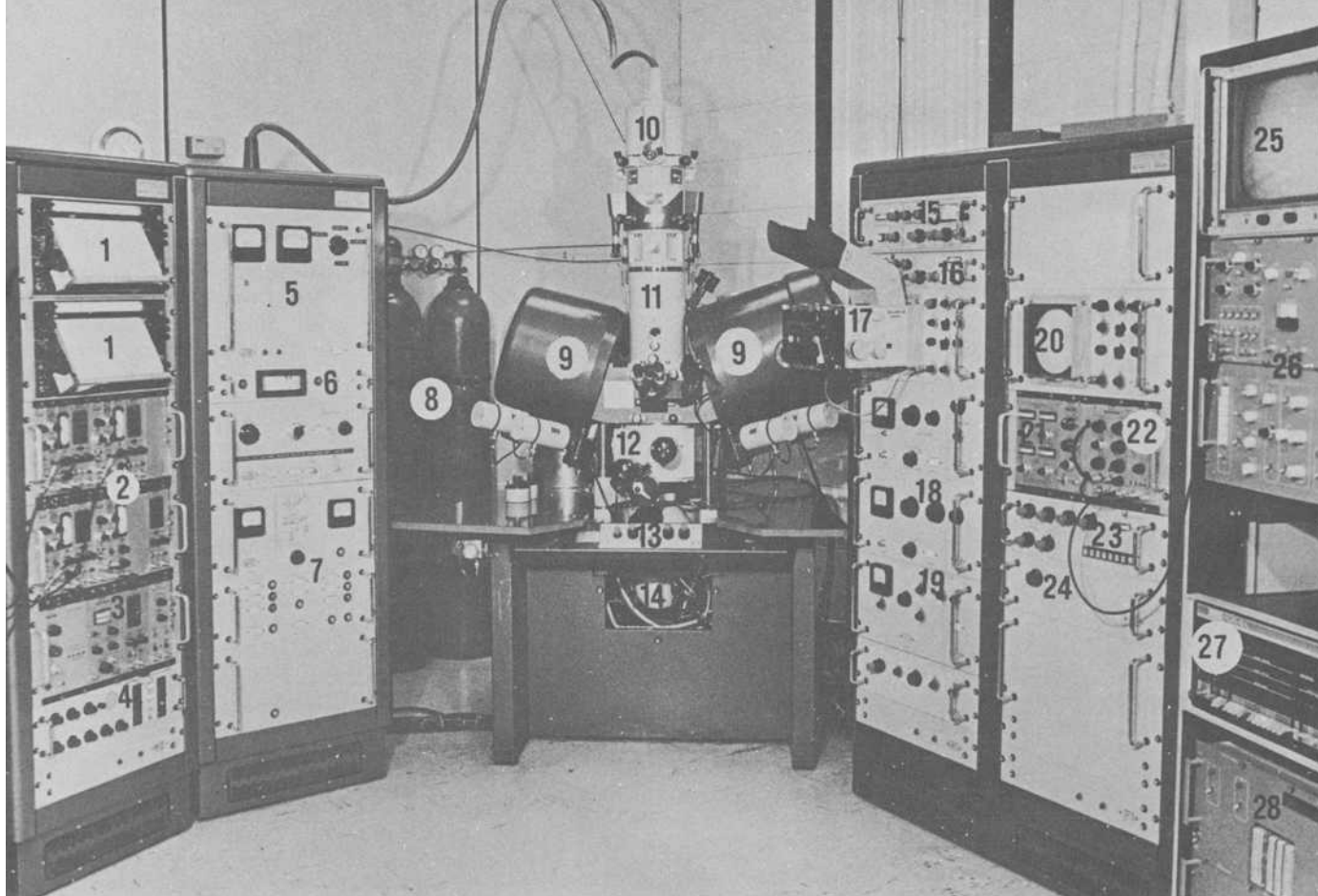


Fig. 1—An electron probe analyzer and associated equipment: (1) strip chart recorder; (2) four X-ray counting channels; (3) current digitizer and printout control; (4) step scan; (5) high voltage power supply; (6) anticontamination controls; (7) vacuum logic; (8) gas supply for flow proportional X-ray detectors; (9) two wavelength dispersive spectrometers; (10) electron gun; (11) electron column; (12) specimen stage; (13) transmission electron microscope (TEM) controls; (14) TEM photographic chamber; (15) nanoammeter; (16) control for secondary and backscattered electron images; (17) Polaroid recording camera; (18) power supplies for condenser and objective lenses; (19) electron beam scanning and deflection controls; (20) display scope for energy dispersive spectrometer (EDS); (21) power supplies for proportional counters; (22) electronics for EDS system; (23) line scan; (24) power supply for light optics; (25) display scope for EDS; (26) multichannel analyzer; (27) PDP8/L computer; (28) tape deck for use with the computer.

metals, plastics, glass, rubber, soft tissue, blood, deep sea nodules, brick, UFOs, carpet fibers, rabbit and human hair, magnetic tape, solvent residues, brake fluids, teeth, bone, gall stones, ceramics, fiber reinforced materials, semi-conductors, corrosion and oxide films, electrodeposits, TFE resin, thin films, coatings, plastic foams, paper, paints, glues, air pollution particles, oils, gas and steam turbine exhaust particulates, and plant leaves.

The Appearance of Combination Instruments/ The microchemical application of the EPA has been so successful that a concerted effort is being made today to incorporate EPA capability into scanning electron microscopes (SEM) and transmission electron microscopes (TEM). Obversely, considerable engineering work has been directed toward adding SEM and TEM capabilities to existing electron probes. The ultimate goal is to be able to determine the chemistry, morphology, microstructure, and crystal structure of a small volume of material all in the same instrument, thereby avoiding the often insurmountable difficulties encountered in transferring that volume from one instrument to another and trying to analyze the identical region in each. The incorporation of several techniques into a single instrument is not a new idea; one such instrument [1] was marketed in 1959, but the venture was not a commercial success.

One immediate outcome of these attempts to develop a

universal instrument is that many investigators with little or no analytical experience are suddenly faced with the same problems that microprobers have encountered and disputed for several years. This review should be most useful to the novice embarking upon what at first glance might appear to be a tortuous journey into the depths of quantitative electron beam microanalysis. Hopefully, all will emerge enlightened and emboldened with the courage to perform such analyses with confidence. The merits and drawbacks of the different instrumental combinations will be presented, in an attempt to aid those faced with the immediate problem of selecting an instrument at a time when claims of superiority for each combination are abundant. The role of associated techniques such as ion mass analysis and Auger electron spectroscopy will also be presented.

The Goals of This Review and an Outline of the Presentation/ The theme throughout will be that of accurate quantitative analysis. A brief review of EPA is followed by a discussion of the features that limit its performance, indicating the knowledge needed to rectify such problems and the manner in which a combined instrument can improve performance. A detailed discussion of the potential of the energy dispersive spectrometer (EDS) is presented, as it opens new horizons for all electron beam analytical instruments. A serious attempt is made to establish the EDS's present and potential capability in quantitative analysis, while also indicating the problems that presently limit its use both qualitatively and quantitatively.

¹Italic numbers in brackets refer to the list of references at the end of this paper.

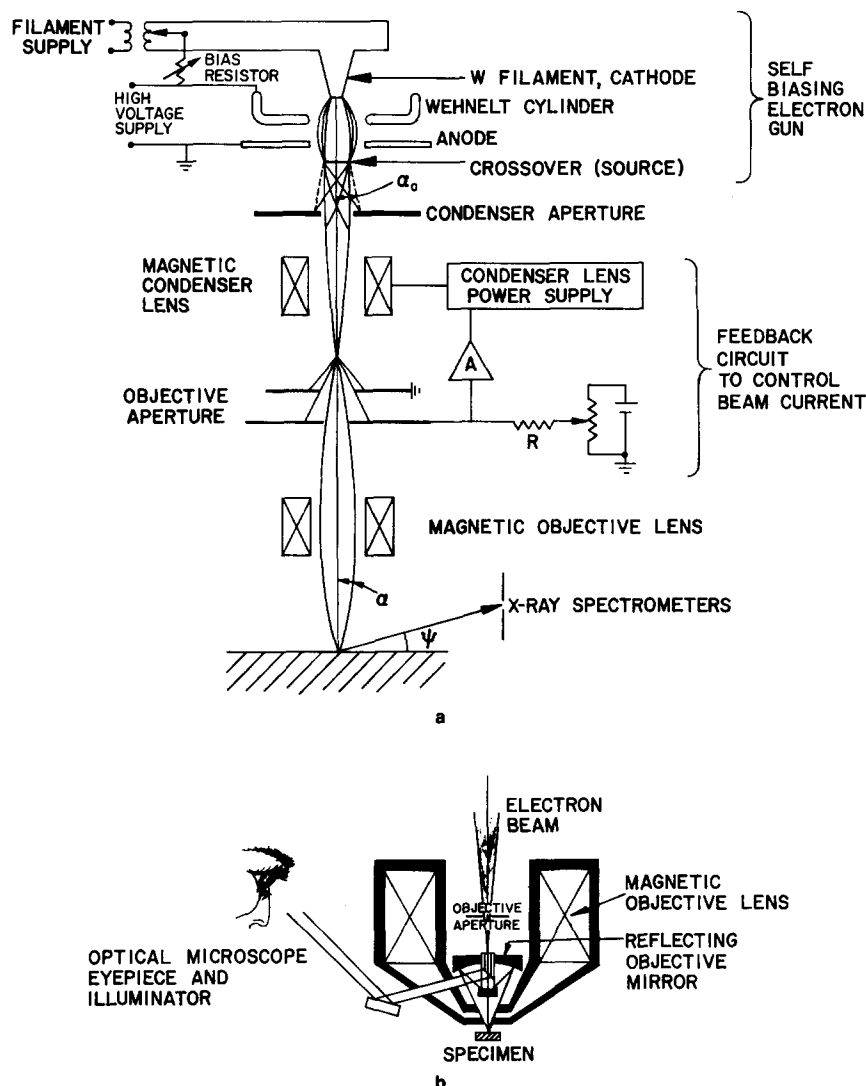


Fig. 2—Schematic drawing of the electron optical system in an electron probe analyzer: (a) the triode, self-biasing electron gun, and other column components; (b) the magnetic objective lens and the geometric configuration of the light optics.

Because the problems encountered in collecting meaningful microanalytical data by all of the methods are similar, regardless of the type of spectrometer or instrument used, a short section on experimental error precedes the detailed discussion of quantitative theory. In the theoretical section, the corrections that must be applied to the raw data are pursued, and the reader is made aware of the lack of complication in the performance of corrections and the reasons for the existing limitations on accuracy. Hopefully, such information will enable the microanalyst to approach his problems not only with a knowledge of the quantitative capabilities of his instrument but also with a thorough understanding of its limitations, expected accuracy and precision, and its resolution and sensitivity capabilities. A complete example problem is presented in an appendix which includes all of the steps and physical data required in a typical analysis of a three-component

system. We should mention here that complete definitions of all the terms (symbols, abbreviations, and units) are given in another appendix, both in the order of their appearance in the text and in alphabetical order, so that the reader can acquaint himself with the terminology of the field before our discussion begins. However, the terms are described throughout the text, so this is not mandatory. Some of the outstanding work that has been carried out with EPA is described in order to acquaint the analyst with the myriad of materials that can be examined.

A list of useful books and outstanding papers is provided to help newcomers through the literature that has built up in recent years. Existing electron probe user groups located throughout the United States, Canada, and Europe are mentioned and are an excellent place for new analysts to get started in this intriguing business of quantitative microanalysis. Before dis-

cussing the complexities of microanalysis it would seem appropriate to make a few historical comments and to indicate the primary areas of usefulness of EPA.

Historical Information/ Moseley [2] was the first to discover the linear relationship between the square root of the X-ray line frequency and atomic number. He realized in 1913 the possibility of chemical analysis through the examination of the X-ray spectrum generated by electron bombardment. It was not until 1949, however, that Castaing and Guinier [3] described an instrument called the "microsonde electronique," or electron microprobe. In his doctoral thesis [4] Raymond Castaing in June of 1951 not only presented the details of the instrument he had designed but also laid the foundation of quantitative analysis.

In 1955 Castaing displayed, at a meeting of the Societe Francaise de Physique, an instrument which served as the prototype for the first commercial instruments, one of which was installed in the research laboratories of the International Nickel Co. in 1958. The original Castaing probe did not possess the electron beam scanning capability which was later developed by Cosslett and Duncumb [5] in 1956 and incorporated into an EPA in 1959 [6]. Birks [7] presents a detailed history of instrumental development in his book indicating the activities of many scientists in the mid 1950's and the work carried on concurrently with Castaing by Borovskii [8] in Russia.

Short Description of the Instrument/ In EPA a beam of energetic electrons in an evacuated column can be focused to a diameter of about $0.3 \mu\text{m}$ at the surface of a specimen. These electrons produce inner shell (K, L, M) ionizations of the atoms. The subsequent generation of characteristic X-radiation can be detected by a crystal spectrometer, which will also indicate the radiation's spectral distribution, and the intensity quantized with electronic counting systems. By rapidly deflecting the electron beam over small areas on the surface, it is possible to observe the spatial distribution of elements within the specimen. The value of the instrument lies in its ability to generate a measurable X-ray intensity in extremely small volumes of material, approaching one cubic micrometer, and, in many cases, provide a quantitative chemical analysis and the identification of all elements with atomic numbers greater than three. While quantitative analysis of metallic specimens is generally not routine, because of the many corrections required to convert measured X-ray intensities to chemical compositions and the care required in the collection of good experimental data, it is usually possible to obtain a relative accuracy in the determined concentration of



Fig. 3—Micrometeorite impact crater in a glass spherule about 0.2 mm in diameter, from Apollo 11. The color scanning X-ray micrograph (SXM) shows the high metallic content, mostly iron with high nickel, associated with the meteorite. Some troilite, FeS, is also present. Color coding: blue→iron; green→nickel; red→sulfur. Magnification: 300. Courtesy of Heinrich [240].

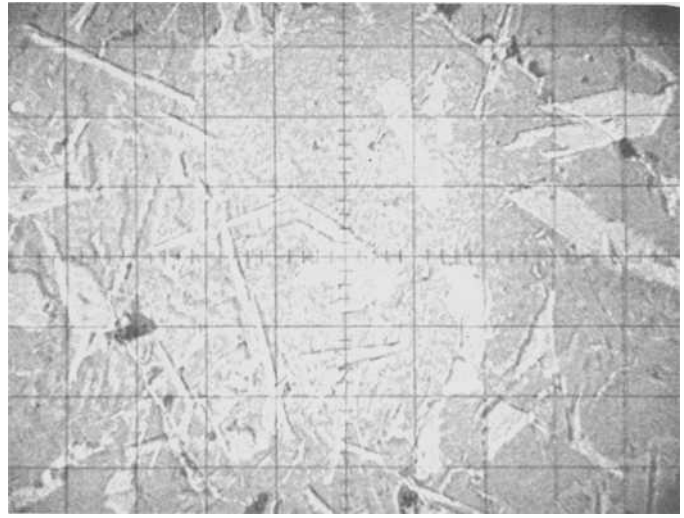


Fig. 4—Scanning electron probe color composite of basaltic rock from Apollo 11. Courtesy of Heinrich [240]. (a) This micrograph shows the presence of two types of silicates and ilmenite. The violet regions indicate silicates containing iron pyroxene; the light blue regions indicate silicates without iron (feldspar), and the orange regions indicate ilmenite. The specimen current image has been blended into the micrograph to indicate microstructure. Magnification: 200.

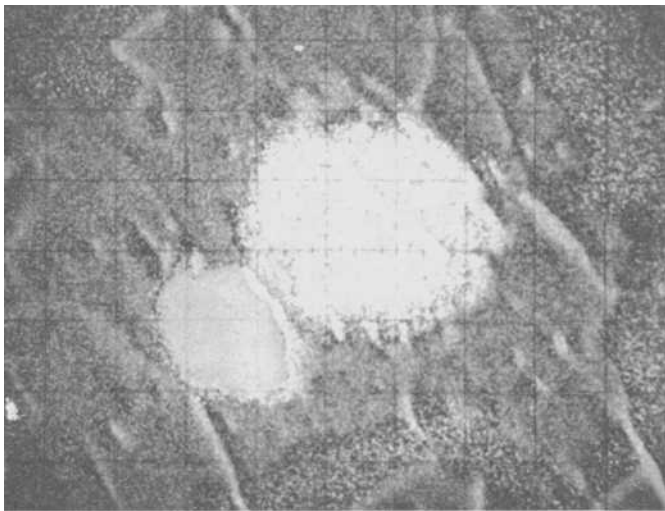
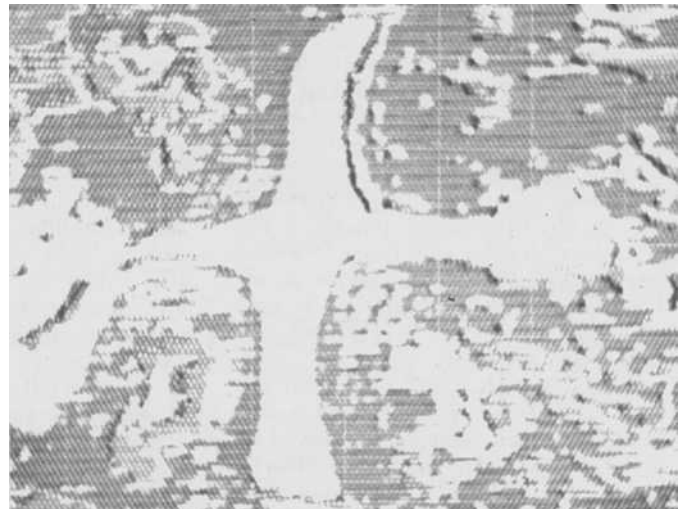


Fig. 4—(b)—This micrograph shows an inclusion of metallic iron (brick red) and one of troilite (FeS). Color coding: red→iron; blue→nickel; green→sulfur. Magnification: 1000.



Fig. 5—Color SXM of terrestrial basalt from Disco Island showing three different silicates. The pink-violet area indicates silicates with calcium and aluminum, the blue-green areas indicate silicate with iron and aluminum, and the orange region indicates silicates with iron and calcium. Color coding: green→iron; red→calcium; blue→aluminum. Magnification: 300. Courtesy of Heinrich [240].

Fig. 6—Multicolor specimen current image of an archaeological bronze artifact from a southern Sumaria site. Color coding: blue→low average atomic number (mostly Cu-Cl corrosion products); reddish-orange→intermediate average atomic number (copper particles); green→high average atomic number (Cu-Sn matrix). Magnification: 750. Courtesy of Ficca [235]. See page 59 for further details on figures 3–6.



NOTE: Original color photographs appear in the November issue of *MR & S*, p. 11.

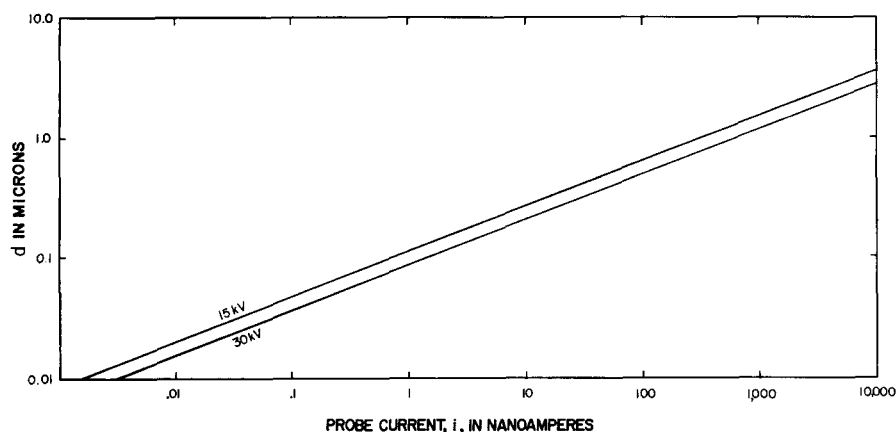


Fig. 7—The geometric electron beam diameter, d , as a function of the beam current at two different acceleration voltages (E_0). The curves are derived from Eq 1 for a typical EPA.

1 to 3 percent of the amount present using pure element standards.

When Can an EPA Be Used Effectively? Throughout the discussion it would be useful to keep in mind the areas to which the instrument can be applied most profitably and also what restrictions apply to the state of the specimen. The ability to maintain a stable electron beam of high current and small diameter makes highly localized chemical analysis possible with a spatial resolution usually in the range of 0.5 to 3 μm and an analytical volume of 1 to 10 μm^3 . Thus, the classical applications of EPA consist of studying on the micrometric level concentration gradients particularly at phase boundaries, surfaces, grain boundaries, diffusion couple interfaces and joined sections; *in situ* inclusion and phase identification (intermetallic compounds); compositional variations within a single phase (segregation); and the identification of contaminants, both foreign to and characteristic of a material. The analysis is quantitative with an expected accuracy of 1 to 3 percent of the amount present when the measured concentration is above 10 percent, when $Z > 10$ (where Z is the atomic number), and when the specimen is carefully polished and flat. This is a remarkable capability considering the fact that the mass of the analyzed element may be in the range of 10^{-14} to 10^{-16} g.

Electron beam scanning (EBS) extends the localized chemical capability to one of chemical distribution on the micrometer level for areas from 20 by 20 μm on up. It is in this scanning mode that the bulk of the past EPA work has been done. The high mass sensitivity (10^{-16} g) that is achieved through X-ray generation and efficient detection permits the accurate analysis of small amounts of material, as in the examination of thin films (well under 100 Å) both isolated and on substrates, liquid and solvent residues, corrosion films,

oxidation and corrosion processes, and surface analyses at depths of 0.3 to about 10 μm . Because the analysis is generally nondestructive, art treasures, rare coins, and criminal evidence can be analyzed. Any element stable in vacuum with an atomic number greater than 3 can be analyzed and the greatest sensitivity is in the range of $Z = 12$ to 30. Elemental rather than structural information is generally provided. The limits of detection are modest and usually range from 50 to 1000 ppm. From this generalized view of EPA and its capabilities let us now progress to a more detailed description.

The Electron Column

General Description/ Figure 1 is a photograph of a modern electron probe installation. Figure 2 is a schematic drawing of the electron column. Electrons released by thermionic emission from the hot (2500 to 3000 K) V or hairpin-shaped tungsten filament (acting as a cathode) are accelerated by an electrical potential (1 to 50 kV) applied between the anode and the filament. In this triode electron gun the Wehnelt cylinder or grid is maintained at a greater negative potential (a bias voltage of a few hundred volts) than the cathode through the use of a variable-bias resistor. This self-biasing configuration provides for a stable emission, permits control of the emission area on the filament, and allows crossover of the electrons. The crossover area consists of a high current density divergent electron beam with a diameter in the range of 50 to 100 μm . The accelerated electrons leave the electron gun at a constant velocity, enter the remainder of the column, which is at a constant potential, and are focused by the electromagnetic condenser and objective lenses. The function of the condenser lens, which has a variable focal length controlled by the lens current, is to vary the

beam current and provide an initial demagnification of the source. As the focal length of the condenser lens is decreased, the transmitted beam current and the beam diameter (image size) decrease. The current decrease is caused by the increased beam divergence on the image side of the lens accompanying the increasing demagnification. An aperture which intercepts a portion of the divergent beam before it enters the objective lens stabilizes the beam current. In our instrument, for example, the intercepted current is used in a feedback loop to vary the condenser lens current (focal length) and thereby maintain a constant beam current. The fixed focal length objective lens further reduces the image formed by the condenser, usually by one fifth to one tenth. The final beam diameter is larger than that of the geometrically reduced source (d_g) because of spherical aberration in the objective lens.

Relationship between Probe Diameter and Probe Current/ In a divergent electron beam the electrons farthest from the optical axis are focused more strongly and thus spherical aberration results. The contribution to the total beam diameter from spherical aberration (d_s) is a function of the lens design and the half angle α , which is the angle between the limiting ray and the optical axis. These quantities are related by the expression $d_s = C_s \alpha^3 / 2$, where C_s , the spherical aberration co-

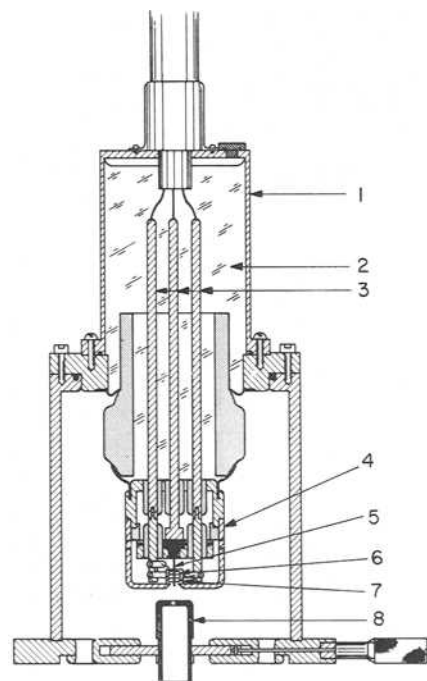


Fig. 8—A schematic diagram of the Broers lanthanum hexaboride (LaB_6) electron gun. The LaB_6 cathode is indirectly heated by the heater coil: (1) oil container; (2) oil; (3) copper cooling rods; (4) Wehnelt electrode; (5) LaB_6 cathode rod; (6) heater coil; (7) heat shield; (8) anode. Courtesy of Broers [14].

efficient, is a function of lens design. Typical values of C_s vary from 3 to 8 cm in an EPA with a working distance of about 1 cm. It is apparent from the above expression that d_s can be reduced by reducing α , which can be reduced by decreasing the size of the aperture of the objective; however, the transmitted current would also be seriously reduced because $i(\text{transmitted}) = i(\text{incident})[\alpha(\text{aperture})/\alpha(\text{divergent beam})]^2$, that is, the transmitted current varies with the square of the aperture angle. The spherical aberration can also be reduced by decreasing the focal length of the lens, but in practice it is necessary to achieve a compromise between C_s and working distance. The need for space for light optics, various types of detectors, etc., poses a practical minimum on the working distance. The electron beam size d , at the specimen surface, is given by

$$d^2 = d_g^2 + d_s^2$$

since the electron distribution in the beam is gaussian [9]. In an EPA the increase in the beam diameter due to chromatic aberration and diffraction effects is negligible. As the focal length of the condenser lens decreases, d_g and the beam current decrease and the relative contribution due to d_s increases. The amount of current, i , in a geometric beam of diameter d_g at the specimen surface is the product of the gun brightness, the area of the beam, and the included solid angle,

$$i = (\beta) \frac{(\pi d_g^2)}{4} (\pi \alpha^2)$$

where β , the gun brightness, is in A/cm²/sr. Using the expression for current density at crossover (from Langmuir [10]), $i_0 e E_0 / kT$ A/cm², and $(d^2 - (C_s \alpha^3/2)^2)$ for d_g^2 , i becomes

$$i = \left(\frac{i_0 e E_0}{\pi kT} \right) \left(d^2 - \frac{C_s^2 \alpha^6}{4} \right) \left(\frac{\pi^2 \alpha^2}{4} \right)$$

where e is the electron charge, k is the Boltzman constant, T is the filament temperature in deg K, E_0 is the acceleration potential in volts, and i_0 is the filament emission current density. Differentiating and solving for the value of α that provides the maximum i results in α (optimum) = $(d/C_s)^{1/3}$ and

$$i = \left(\frac{i_0 e E_0}{\pi kT} \right) \frac{3\pi^2}{16} \frac{d^{8/3}}{C_s^{2/3}} \quad (1)$$

Others [11, 12] have used $d = d_g + d_s$, in which case the constant $(3\pi^2/16)$ becomes $9\pi/64$ and α (optimum) = $(d/2C_s)^{1/3}$. A typical value of i_0 for a W filament is 2 A/cm² at 2700 K. The theoretical value of gun brightness cannot be attained in practice because the value of $i_0 e E_0 / \pi kT$

Table 1—The Characteristics of Electron Guns with Different Cathodes

Cathode	W hairpin	LaB ₆	LaB ₆	W field
Tip diameter	.005"	20 μ	1 μ	500 $\text{\AA}$
Probe diameter ($\text{\AA}$)	50	30	25	10
Probe current (amperes)	8×10^{-13}	1×10^{-12}	2×10^{-12}	1×10^{-10}
Brightness (10^6 amp/cm ² /sterad)	0.07	1	6	200
Operating temp. (°K)	2859	1970	2000	ambient
Vacuum required (torr)	5×10^{-4}	1×10^{-5}	1×10^{-6}	1×10^{-9}

* from A. Broers (Ref. 23)

used corresponds to the maximum for the gaussian distribution at crossover; therefore, rather than achieving 83,000 A/cm²/sr, values close to 60,000 A/cm²/sr are encountered. Figure 7 is a plot of i versus d for E_0 values of 15 and 30 kV in an EPA.

Improvements in Sensitivity and Resolution/ The electron gun produces an intense, stabilized, focused source of high energy electrons. This enables the operator to focus a sufficient amount of current at the specimen surface to create an intense X-ray point source. Efficient detection of this fine source makes electron probe analysis a reality. The spatial resolution of the technique depends to a large extent upon the beam current, while the sensitivity (counts per second (cps) per unit current i) depends primarily upon the detection system. Thus, improvements in the detection system allow the use of lower currents, which in turn result in improved resolution, while increases in current at constant beam diameter result in better sensitivity. Detection improvements using solid state detectors will be discussed later. Most commercial EPAs available today provide sensitivities in the range of 500 to 1200 cps/nA on pure Cu and have minimum d values of 0.1 to 0.5 μ m.

Spherical Aberration, C_s —How can the current in an electron beam of given diameter be increased? Reduction in the spherical aberration of the objective lens has not been accomplished owing to the fact that the working distance of the final lens must be large enough to accommodate the required detectors and X-ray spectrometers. In addition, significant improvements in C_s that would require radical changes in lens design provide small increases in current, for example, a reduction in C_s of one half (a difficult feat indeed) increases i by a factor of only 1.6.

Gun Brightness—Other than E_0 , which is established within relatively narrow limits depending on the analytical problem, the only possibility remaining in Eq 1 is an improvement in gun brightness. The

thermionic emission current density, i_0 , increases rapidly with temperature because $i_0 = AT^2 \exp(-B/kT)$, where B is proportional to the filament material work function and A is a material constant. The filament life diminishes rapidly through sublimation, so a practical limit of about 2700 K exists on the operating temperature of a W filament. This corresponds to a current density of about 2 A/cm² and a gun brightness of about 60,000 A/cm²/sr. For a C_s value of 3.5 cm, currents of about 1 μ A and 2nA at 30 kV are the maximum in 1 and 0.1- μ m probes, respectively [13]. Improved brightness would provide the same sensitivity with better resolution (lower current or accelerated potential) or the same resolution with better sensitivity. Note, however, that to maintain a constant intensity while reducing the beam diameter requires large increases in brightness. Duncumb [9] has found that the count rate is proportional to the product of the brightness and the size of the X-ray source raised to the 4.4 power under conditions corresponding to the optimum resolution for a given count rate.

LaB₆ Thermionic Cathode—The unique and highly promising gun configuration shown in Fig. 8 has been developed by Broers [15]. The pointed (1- μ m diameter) lanthanum hexaboride (LaB₆) thermionic cathode is heated either by radiation or by electron bombardment from the W coil circumscribing, but not touching, the cathode. Broers and Brandis [16] have achieved a gun brightness of 560,000 A/cm²/sr at 12 kV and estimate a two-fold increase in resolution, an increased current capability of 5 to 10 times for a given beam diameter, and several thousand hours of filament lifetime. The emission is stable and the gun can be incorporated into existing instruments. Koopman [17] reported that the resolution improved from 200 $\text{\AA}$ to 75 $\text{\AA}$ when the conventional gun was replaced by a Broers gun. Separate pumping of an isolable gun chamber provided stable emission and continued high performance. Two SEM

manufacturers have recently made available the Broers gun for use on their SEMs [18]. Wolter and Sanders [19] described a directly heated LaB₆ gun that required a power input of 10 W, compared to the 60 W required for the indirect heating configuration by Broers, provided a source brightness of 100,000 A/cm²/sr at 15 kV, and had an estimated lifetime of 3000 h.

Coated Cathodes—Coated cathodes have not been successful in electron guns in the past, presumably due to inadequate performance caused by inactivation in the poor vacuum normally encountered (10⁻⁵ torr). Albert et al [20] have developed sintered powder cathodes which exhibit emission densities (brightness × solid angle) 5 to 10 times as great as those of standard W filaments. They electrolytically etch a standard W filament to remove 30 to 40 percent of the diameter and then dip it into a mixture of fine powders (90 percent W (3.5 μm), 9.5 percent Th, and 0.5 percent Zr) held together by an amylacetate nitrocellulose binder. Sintering at 1300 to 1400 C gives the metallic coating a thickness of about 0.005 in. In an electron microscope, a current density of 10 A/cm² was obtained at about 1650 and 2650 C for the W-Th-Zr coated W and a pure W cathode, respectively [20]. Thousands of hours of cathode life are predicted at the lower operating temperature. Gransden and Beaman [21] have been able to obtain marginal improvements with similarly coated cathodes. They found a reduction in X-ray source size of 0.25 μm at 100 nA and 25 kV in Ni; however, filament lifetime was not improved, owing to difficulties in filament construction.

Field Emission Source—Crewe et al [22] have developed an electron gun based on a field emission source. The source is a pointed W tip (~500 Å radius). Emission stability is satisfactory only in high vacuum (10⁻⁹ torr), and the current carrying capabilities are only superior to a conventional W filament when the beam size is below 2000 to 3000 Å; however, large improvements in brightness are possible in small beams (below 1000 Å) as indicated in Table 1, extracted from the paper by Broers [23]. A manufacturer has just announced the availability of a SEM equipped with a field emission gun. The W filaments presently used in SEMs limit their resolution because, as the beam size drops below 100 Å, it is not possible to generate enough current in the beam to produce a satisfactory image.

Thermionic Field Emission—Castaing [12] referred to the use of thermionic field (TF) emission where, under the action of an extraction field, the filament would be heated to temperatures just below the emission temperature; however, no further reports on TF guns have appeared.

Thermionic pointed filaments have been tried, usually in TEMs, but with marginal success primarily because of sporadic reliability and short lifetime.

Tetrode Electron Gun—In 1967, Kanaya et al [24] reported on a tetrode electron gun in which two grids rather than one, as in the standard triode configuration, were used in the construction of an X-ray microfocus unit. At 30 kV, a 10-μm X-ray source with a beam current of 150 μA was obtained for an emission current of 600 μA. To our knowledge no further information concerning such a gun has been published and the current density attainable in a small probe is unknown.

As far as gun design is concerned, the Broers gun, while not inexpensive, offers immediate gains in performance. The increased brightness may in special cases (low thermal conductivity) result in thermal loading problems, but this will generally not be a limitation.

Lens Design/ While it is apparent that significant improvements in gun design will be incorporated into new instruments, possible improvements in the electron optical system are less evident.

Minilens—Duncumb [25] has reviewed the use of the minilens developed by LePoole [26] in which the conventional iron shield and pole pieces are eliminated. In this lens the conical bore diameter is only 1 to 3 mm and the coil is wound on a thin nonmagnetic former. With a 5-cm-diameter minilens it is possible to attain the same optical properties as in a conventional objective lens 10 cm in diameter. Several advantages accrue from the small diameter. In a normal electron incidence configuration a considerably higher X-ray take-off angle is possible simply because of the reduction in diameter. The small size also leaves more room for accessories in close proximity to the specimen.

Fontijn et al [27] have constructed an EPA using the minilens to good advantage. Since the electron column (electron optical axis) is tilted at a 45-deg angle to the horizontal specimen surface, it is possible to observe the specimen through a vertically mounted, high quality microscope which is not located within the probe forming column and is external to the vacuum system. Present spectrometers are mounted to provide a 30-deg take-off angle, but any take-off angle between 0 and 60 deg is possible depending on spectrometer design. If the light microscope were replaced by a spectrometer, a 90-deg take-off angle would be possible.

Cooke and Duncumb [28] have constructed an EPA-TEM combination in which the minilens serves as the objective lens for the EPA and is actually partially located within the electron microscope objective. More details of this type of in-

strument will be presented later. Chapman [29] has used the minilens to develop an accessory which makes it possible to perform microanalysis in a TEM with a minimum beam diameter of 0.25 μm. To date no EPA or SEM manufacturer has incorporated a minilens into a commercial instrument. The reason may be that the optimum lens design has yet to be established.

Flat Lens—Bassett and Mulvey [30] have discussed different geometries of iron-free lenses and concluded that a thin (flat or pancake) lens might be the most desirable. With such a lens a helical winding is used and the electrons can be focused above or before the lens. This negative working distance allows an unlimited choice of X-ray take-off angles; if focused below the lens, high take-off angles are also possible.

Stability of the Beam Current and Beam Position/ The alignment of the electron beam is easily accomplished through simple filament and aperture positioning and adjustment of the lens currents. As far as the electron column is concerned, the stability of the beam current and position are of primary importance. Recent tests on several commercial instruments revealed that most existing instruments possess good beam stability [31]. Fitzgerald [32] has written a definitive article discussing stability problems, which indicated the regulation required on objective and condenser lens currents and acceleration potential to provide beam position stability to within 0.1 μm and beam current stability to within 0.1 percent. Reed [33] has reported on the effects of gun parameters on stability in an EPA. Variations in the gun high voltage, bias voltage, filament current, lens currents, filament position, and aperture position can result in beam instability. The long term stability (several hours) needs to be improved to facilitate more sophisticated experimentation and to allow computer control of the instrument. Electronic alignment should be instituted and the alignment should be maintained when the acceleration potential is altered.

Electron Interactions in Solids

Before discussing the detection of the emitted X-radiation, let us consider the analytical resolution attained in practice, which is often considerably greater than the beam diameter at the specimen surface, d in Eq 1. The distribution in depth of generated X-radiation is dependent upon the manner in which the impinging electrons are scattered and absorbed throughout the depth. Unfortunately, fast electrons impinging upon a solid target encounter an extremely complex environment. The impinging electrons undergo elastic (change of direction with negligible

energy loss) and inelastic (change of direction with energy loss) interactions with the atomic nucleus and the bound atomic electrons. For the purposes of microanalysis there are four possibilities to consider: (1) elastic scattering by the atomic nucleus—negligible energy loss but significant deviation from the incident direction; (2) elastic scattering by the bound electrons—negligible; (3) inelastic interaction with the atomic nucleus—this corresponds to the emission of radiation by a moving electron in the coulomb field of the nucleus, that is, the emission of white or Bremsstrahlung radiation; (4) inelastic interaction with the bound electrons—discrete energy loss usually resulting in ionization of the atom by the removal of the loosely bound outer electrons and, infrequently, of an inner shell electron. In the energy range of concern in microanalysis (1 to 50 keV), the first and last interactions are the predominant ones.

Shape and Size of Excited X-ray Volume/ Elastic scattering by the nucleus is by far the most prevalent event, because the electron mass is easily deflected by the nucleus even at considerable distances from the nucleus. Cosslett and Thomas have published a series of outstanding papers [34–39] correlating existing scattering theory with their experimental data. They describe four stages of scattering. (1) single scattering characterized by a single high angle ($\theta > 90^\circ$) scattering act, that is, Rutherford scattering by the atom; (2) plural and (3) multiple scattering during which the electron undergoes a series of small angle scattering acts, which result in the gradual deviation of the incident electron from its initial direction; and (4) diffusion scattering characterized by the random movement of the electron.

The studies on thin films by Cosslett and Thomas have revealed that plural scattering [34] involves on the average about ten elastic scattering acts, multiple scattering [35] sets in after about 20 events, and diffusion scattering [38] after 100 ± 10 events. By measuring the angular distribution of electrons transmitted by thin films, Cosslett and Thomas [35] have determined the most probable angle of total scattering for the different scattering regions, 38° deg in diffusion scattering. Figure 9 from Cosslett and Thomas [35] is a plot of the fraction of transmitted electrons as a function of the film mass thickness (ρx) for Cu and Au films. Diffusion is established much earlier in the range at higher atomic number and this dependence on Z increases as the energy (E_0) increases. At 20 kV diffusion is established after the electron has traveled 25 and 65 percent of the range in Au and Al, respectively. The range R , and thus the penetration, has been found to be primarily dependent

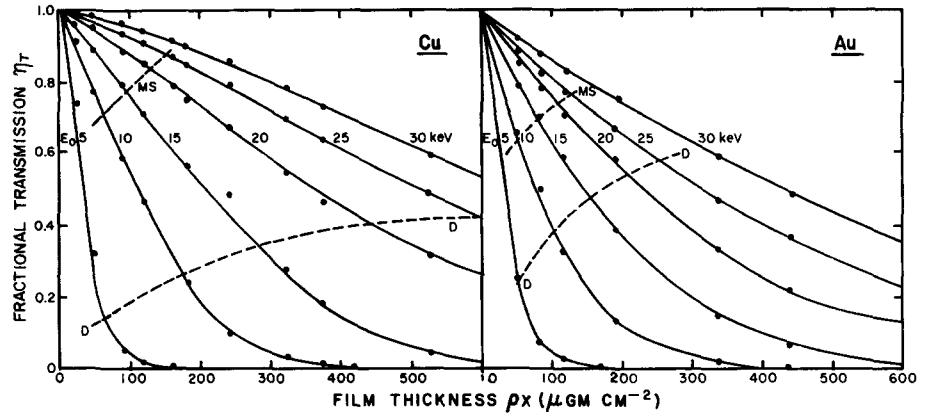


Fig. 9—The fractional electron transmission, η_T , as a function of film mass thickness. Data are shown for thin films of Cu and Au. MS represents the transition from plural to multiple scattering and D represents the transition from multiple scattering to diffusion scattering. Data from Cosslett and Thomas [35].

on energy [39]. As will be shown, the total spread or deviation from the incident direction is often taken to be the penetration.

The scattering cross section at constant energy varies with Z^2 . The probability of scattering through an angle varies as Z^2/E^2 . Thus, the diameter of the excited volume is primarily a function of energy and the shape is primarily a function of atomic number. A qualitative picture evolves: For low atomic numbers there is not much early scattering near the surface of the specimen. As the electron penetrates and loses energy the scattering increases, but at that depth at which complete diffusion is established, the electrons have penetrated to such an extent that they cannot escape. Thus, there is little backscattering and what little does occur is the result of early single scattering events. Diffusion is established late in the range. This explains the commonly depicted teardrop electron distribution for light elements [40]. As the incident energy increases the shape remains unchanged but the penetration (and hence diameter) increases, resulting in increased size. In a heavy element there is considerable scattering ($\propto Z^2$) near the specimen surface, diffusion is established early in the range and a considerable amount of backscattering is possible through plural and multiple scattering. This leads to a nearly hemispherical electron distribution for heavier elements [40].

Theoretical Expressions for Lateral Electron Spread/ In order to predict the X-ray resolution the lateral electron diffusion must be known. Experimental range values are obtained from measurements of electron transmission through (maximum and extrapolated range) and energy losses in (mean range) thin films and thus are related to the penetration. Theoretical range expressions can be simply obtained by integration of an energy loss expression, such as that of Bethe [41] where

$$\frac{dE}{dx} = -2\pi e^4 \frac{N_0 \rho}{A} Z \ln \left(\frac{1.166E}{J} \right) \quad (2)$$

where J is the mean ionization potential, N_0 is Avogadro's number, A is the atomic weight, and ρ is the target density. The Bethe range, R_B , is obtained by integrating

$$R_B = \int_{E=E_0}^{E=0} \frac{1}{dE/dx} dE$$

In X-ray generation the energy range of interest is $E = E_0$ to $E = E_c$, the excitation potential for the atomic level of interest. Defining the stopping power as $S \equiv -dE/\rho dx$ and the range as $R = \int dE/\rho S$, Castaing [12] used the Webster [42] expression for S , where

$$-\frac{dE}{\rho dx} \equiv S = \frac{8.87(10^4) Z}{E^{0.7} A}$$

This leads directly upon integration to

$$R = 0.033(E_0^{1.7} - E_c^{1.7})A/\rho Z \mu m \quad (3)$$

Castaing [12] assumed the X-ray resolution to be $R_x = R + d$ where $d^2 = d_g^2 + d_s^2$.

Duncumb [9] let the lateral spread equal the penetration when $E = E_c$ and from the Thompson-Whiddington law ($E_0^2 - E_c^2 = 8(10)^{11} A \rho x / Z$, where x is the film thickness) obtained $R = 0.025(E_0^2 - E_c^2)/\rho$. Setting $R_x^2 = R^2 + d^2$ Duncumb [9] found

$$\begin{aligned} R_x (\text{minimum}) &= 1.5d_g = 2.5d_s \\ &= 1.6R = 0.040(E_0^2 - E_c^2)/\rho \quad (4) \end{aligned}$$

where ρ is in g/cm^3 , E is in keV, and R is in μm . Thus, under optimum conditions the X-ray resolution is 1.6 times as great as the contribution from electron scattering alone.

Reed's [43] expression for electron scattering R is based on the experimental voltage dependence found by Cosslett and Thomas [36], where $R = kE_0^n$ with $n = 1.2$ to 1.7 depending on the definition of the range. Reed [43] found

Table 2—Theoretical and Experimental Values for Electron Diffusion and X-ray Resolution

Principal author	Ref. No.	Expression for electron spread or penetration ⁵	X-ray resolution, R_x , or experimental data			
Castaing ¹	12	$R=.033 (E_o^{1.7}-E_c^{1.7}) A/\rho z$	R+d			
Castaing		$R=.076 (E_o^{1.7}-E_c^{1.7})/\rho$	R+d; using $A/z=2.3$			
Duncumb ¹	9	$R=.025 (E_o^2-E_c^2)/\rho$	R^2+d^2 ; 1.6R			
Reed ¹	43	$R=.048 (E_o^{1.5}-E_c^{1.5})/\rho$	$\leq 4.5(1.6R)$			
Andersen	44	$R=.064 E_o^{1.68}/\rho$	expt. penetration-SiO ₂ on Si			
Andersen	44	$R=.0097 E_o^{2.12}/\rho$	expt. spread Si-SiO ₂			
Colby	45	$R=.033 E_o^{1.5} A/\rho z$	expt. penetration Al on Si			
Cosslett	39	$R=k'E_o^n$	mean energy range, $n=1.5$ and $k'=.0096$ for Cu			
		<u>Experimental or calculated values of electron spread or penetration: microns in Cu at indicated E_o.</u>				
		<u>30kV</u>	<u>25kV</u>	<u>20kV</u>	<u>15kV</u>	
Shinoda	46,47	2	1.6	1.0	0.6	R+d
Beaman		2.0	1.6	1.2	1.0	R+d (94%)
Philibert	11			0.7 ²	0.4 ³	R+d
Russ	48	0.6 ⁴			0.3 ⁴	R+d
Bomback	49	0.4				R+d
Bethe	11	2.7	1.9	1.1	0.4	

1) Assumes total lateral spread=electron penetration; 2) 18.3 kV; 3) 15.2 kV; 4) measured on Fe; 5) R is in microns for E_o in kV and ρ in gm/cm³.

$$R = 0.048(E_o^{1.5} - E_c^{1.5})/\rho$$

Using the Duncumb ($R_X = 1.6R$) relationship, Reed defined the qualitative resolution as $0.077(E_o^{1.5} - E_c^{1.5})/\rho$, where the qualitative X-ray resolution is related to the smallest separation at which two objects can be distinguished in a scanning picture, as compared to the quantitative resolution defined by Reed as "the maximum size of object required for 99 percent of the total characteristic X-ray production to take place in the object itself." Reed provides a nomogram for calculating the qualitative resolution and stresses the very important fact that not only does the resolution depend on d and electron scattering but also on secondary fluorescence, that is, X-ray intensity is generated by the continuous spectrum created by the primary beam and also in some cases by other characteristic X-radiation in the specimen. The outcome of the Reed [43] calculation is a quantitative resolution that extends the limits up to 4.5 times his qualitative resolution. Several expressions for the lateral spread R are tabulated in Table 2 along with some experimental values.

Experimental Measurements of Lateral Electron Spread/ In Fig. 10 the spread due to electron scattering in Cu is plotted as a function of acceleration potential for (1) the four theoretical expressions just mentioned (Bethe, Duncumb, Castaing, and Reed); (2) four expressions based on experimental results (Cosslett mean range, Colby, Andersen); and (3) several isolated experimental or theoretical values (Shimizu, Philibert, Russ, Bomback, Beaman). Reasonable agreement between theory (Duncumb, Castaing, Philibert, Andersen penetration) and some experimental values is observed (Shinoda, Beaman). The spread of 0.6 to 0.4 μ m obtained by Russ and Kabaya [48] (on Fe) and Bomback [49] (on Cu-Ag), respectively, in SEMs where d can become negligible are much lower than the theoretical values based on the assumption that the total spread and penetration are equivalent. It is significant that most experimental measurements of the spread (omitting beam size) are lower than the experimental or theoretical values of penetration. Bomback [49] has described an effective method for evaluating the

relative contributions of the beam diameter and electron spread R which consists of simultaneously monitoring the secondary electron signal (d) and X-ray signal (R_X) as the beam traverses a polished interface. Additional work of this nature is needed covering a range of atomic numbers, acceleration potentials, and beam currents, with care being taken to eliminate the effects of backscattered primary electrons.

Figure 11 is one we use routinely to estimate the contribution to total resolution from electron scattering. Table 3 taken from Shinoda [46] lists values for different ranges, penetration values, and lateral spreads in Cu at 30 kV. These values provide a useful picture of the process of electron interaction in solids as it effects microanalysis. Figure 12 depicts some of the different ranges and emphasizes the fact that the X-ray resolution can be considerably greater than the electron beam diameter and often even greater than that expected from primary X-ray excitation.

Henoc et al [50] have performed some outstanding theoretical work and have confirmed the latter finding by careful experiments in which the apparent con-

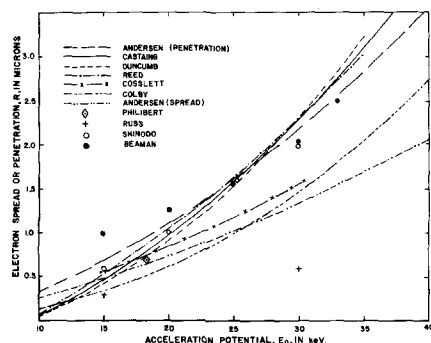


Fig. 10—The lateral electron spread, R , in Cu as a function of the electron acceleration potential, E_0 . The smooth curves were obtained from the expressions proposed by the different authors listed in Table 2. The points represent experimental values measured by the authors indicated. The Reed curve was calculated assuming a lateral spread equal to $3.1 \times$ Reed's R value.

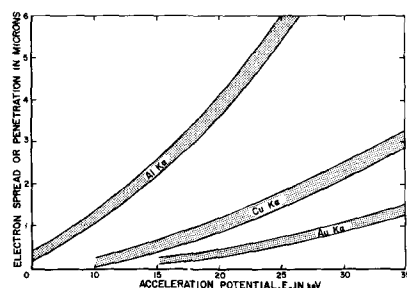


Fig. 11—The lateral electron spread, R , as a function of acceleration potential, E_0 , for Al, Cu, and Au. The bands represent an expected range of values based on theory, experiment, and experience. The expected X-ray resolution, R_x , can be estimated assuming $R_x^2 = R^2 + d^2$.

centration is measured in binary couples as a function of the distance of the primary electron beam, including the electron spread, from the couple interface. Some of these results for $K\alpha$ lines listed in Table 4 illustrate the significant effects of fluorescence, for example, $5 \mu\text{m}$ from the Y-Mo interface in the Mo, 6 wt. percent Y is still measured. It is clear that, when analytical conditions promote such effects, a significant loss in resolution will occur. Perhaps then it is not so surprising that after many years of electron probe analysis it is still difficult to state exactly what spatial resolution will be possible in every material under all possible operating conditions. The complexity of electron scattering in solids, combined with secondary fluorescence effects, eliminates the possibility of a simple solution. In addition, experimental measurements are indirect and not easily performed or interpreted. Our own measurements at the edges of thin films indicate less scattering than predicted theoretically.

Improvements in resolution, when required in practice, are most commonly achieved by low voltage operation, that is,

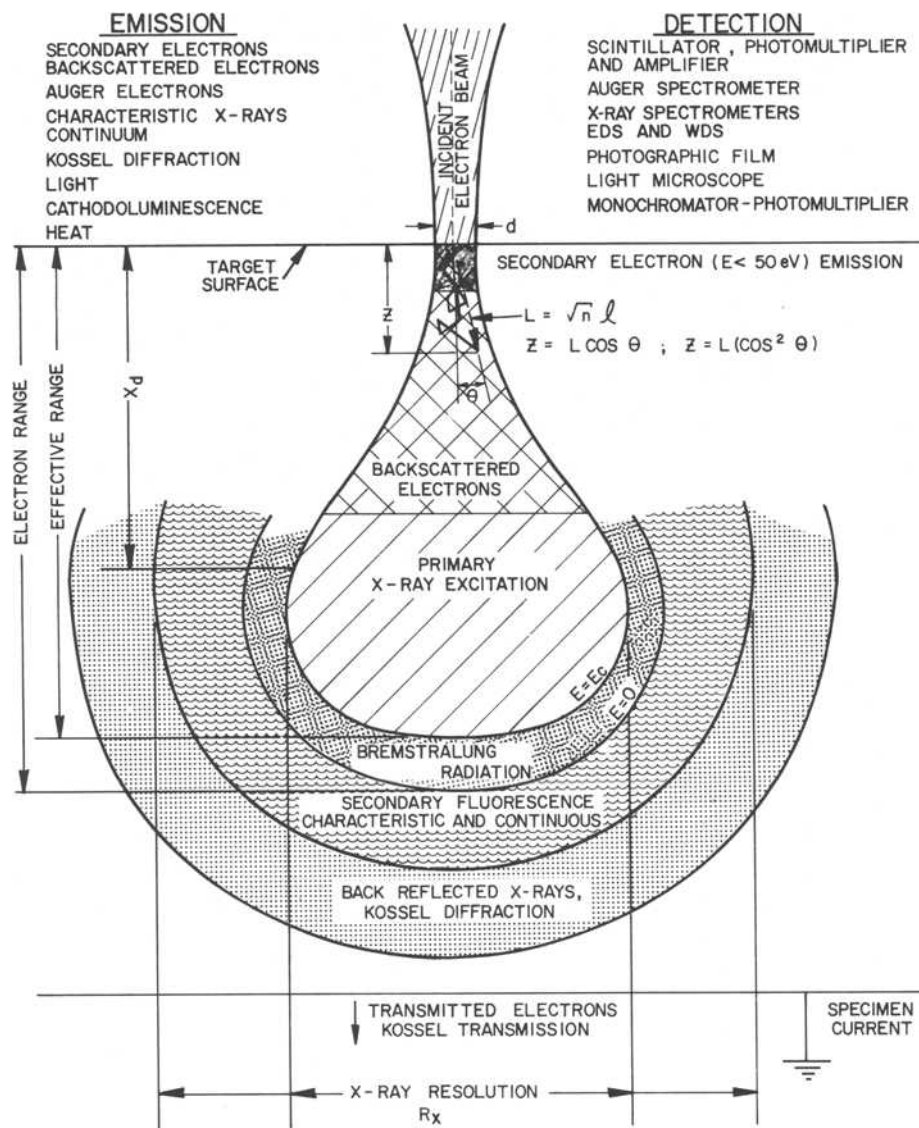


Fig. 12—A schematic representation of the interaction of an electron beam with a solid of moderate to low atomic number. Most of the different signals emitted, their means of detection, and the diameters of the excited volumes from which they originate are shown. L is the mean free path, n the number of events, l the distance traveled between each event, E the average energy of the impinging electron, and X_d the depth where complete electron diffusion occurs.

by allowing E_0 to approach E_c . The accompanying reduction in peak intensity, P , and peak to background ratio, P/B , can often be tolerated. In some cases the use of a longer wavelength X-ray line (L or M) will provide the required resolution and intensity at a low acceleration potential.

Wavelength Dispersive Spectrometers

Enhanced gun brightness coupled with column design improvements will provide a more intense X-ray source, which, in turn, will lead to higher sensitivities (cps/i), lower detectability limits, improved precision, better spatial resolution, and faster scanning speeds. Further gains will be possible if the X-ray detection

efficiency can be increased by improvements in crystals, detectors, or spectrometer design. The most remarkable improvement of the past several years was the energy dispersive spectrometer, which uses a solid state (Li drifted Si) semiconductor detector in conjunction with a multi-channel analyzer. Before considering these devices, let us briefly discuss some of the less dramatic and more conventional approaches to improving detection efficiency.

Fully Focusing and Semifocusing Spectrometers/ In a conventional wavelength dispersive spectrometer (WDS) the emitted X-rays, after undergoing Bragg diffraction ($n\lambda = 2d \sin \theta$; the order of diffraction is n , λ is the radiation wavelength, d is interplanar spacing in the diffracting crystal, and θ is the Bragg angle) by the crystal,

Table 3—Important Geometric Parameters for Electron and X-ray Distributions in Cu at 30 kV (from Sinoda et al., Ref. 46)

Measured parameter	Microns
Electron beam diameter	1.0
X-ray source diameter	3.0
Electron scattering or lateral spread	2.0
Extrapolated range	1.6
Total range	2.2
Depth of complete diffusion	0.9
Depth of maximum x-ray production	0.3
90% of primary x-rays from less than	0.9
90% of backscattered electrons from less than	0.6

Table 4—Apparent Concentration in Binary Couples Caused by Secondary Fluorescence (Henoc, Ref. 50)

Binary couple	Analyzed x-ray line	kV	Cause of fluorescence ¹	Apparent concentration in wt.% at indicated distance from binary couple interface ²		
				0μ	5μ	10μ
Nb-Zr	NbKα	30	CF	5	3	1.7
Nb-Zr	ZrKα	30	CF+NbKβ	6.5	3	2
Cu-Ni	CuKα	25	CF	1.3	.3	.1
Cu-Ni	NiKα	25	CF+CuKβ	2	.5	.2
V-Ti	VKα	18	CF	.6	.1	.06
V-Ti	TiKα	18	CF+VKβ	1	.2	1
Y-Mo	YKα	29	CF+MoKα, Kβ	10	6	4
Ni-Zn	NiKα	25	CF+ZnKα, Kβ	6	2	1

1) Apparent concentration as a result of continuous fluorescence, CF, and the indicated characteristic fluorescence; 2) the electron beam is positioned on the side of the couple containing the unmeasured element.

enter a proportional X-radiation detector. Johann and Johansson focusing spectrometers have generally been used because of their high efficiency and resolution. In both configurations the crystal is bent to a radius of $2R$, where R is the radius of the focusing (Rowland) circle on whose circumference the crystal and counter both move, while the source remains stationary at some point also on the circle. In the Johann arrangement, only the center of the crystal is on the focusing circle and perfect focusing is not possible. In the Johansson arrangement, since the crystal is also ground to a radius R , the entire crystal surface lies on the Rowland circle, focusing on the circle is attained, and a large portion of the crystal provides useful diffraction.

The most common spectrometer configuration today is a linear one in which

the crystal moves along a line passing through the fixed X-ray source. The X-ray take-off angle is constant, the center of the Rowland circle rotates about the source, and the detector does not always lie on the focusing circle. The slight departure from fully focused conditions is not a problem when high quality crystals are used with a wide acceptance slit or window at the detector. The linear spectrometer provides high efficiency, exhibits excellent revolving power, has a constant take-off angle, occupies a small volume, can accommodate a large range of Bragg angles, is easily aligned, and can be mounted coplanar with the electron beam. Semifocusing spectrometers, in which the crystal is close to the source and rotates about a fixed axis, as does the detector, and those where the crystal (mica) curvature

is adjusted to satisfy the focusing requirements ($n\lambda = d \sin \theta$), are in limited use today.

In most cases, for a fixed spectrometer design, the sensitivity can be improved by increasing the X-ray take-off angle, Ψ , which reduces the effective absorption path length in the specimen. This is particularly beneficial for long wavelength radiation. Further discussion of ψ will be found in the discussion of quantitative analysis. Many manufacturers have moved toward higher ψ values, as evidenced by the following, where the manufacturer's name is followed in parenthesis by two ψ values, the first in their originally designed and the second in their presently available instruments: Cambridge (20, 75), CAMECA (15 to 17, 18), JEOL (15, 40), Hitachi (10, 38), Phillips (15.5, 41), MAC (38.5), ARL (52.5). Undoubtedly, any newly designed instrument will have a high ψ (over 35 deg) or a dual ψ (as in Phillips, 15.5 and 41) or a variable take-off angle capability.

Crystal Performance/ The trend in instrumentation has been toward an increasing number of spectrometers and crystals to permit multielement analyses and to provide the best sensitivity and resolution possible at each wavelength. In our instrument, for example, four spectrometers and six crystals have replaced the two spectrometers and two crystals in earlier models. The measured performance of a crystal depends upon the spectrometer design, the radius of the focusing circle, the diffraction plane spacing, the detector, the temperature, the spectrometer alignment, the pressure on the crystal, and the quality of the particular crystal (surface condition, internal stress, etc.). The selection of the proper crystal depends upon the instrument available and the analytical problem.

In electron beam scanning (EBS) work, high intensity and less than optimum resolution are often required, the latter to avoid defocusing effects when the beam leaves the focusing circle. On the other hand, in the measurements of low concentrations the need is to optimize $P \times P/B$, while, in complex alloy systems or bonding studies, the primary need may be high spectral resolution. Poole and Martin [51] have made a thorough examination of the literature and calculated the average intensity performance relative to mica for several crystals used in EPA. These ratings are included in Table 5, where most of the crystals that could be used in EPA are tabulated. The most commonly used crystals are marked with an asterisk.

Some of the more esoteric crystals have not lived up to expectations. The predictions for OHM [52] have failed to materialize. The multilayered sandwiches, consisting of alternating thin films of scattering

Table 5—Diffracting Crystals for Use in Wavelength Dispersive Spectrometers

Crystal designation and/or crystal name	Reflecting planes	2d spacing (Å)	Approximate useful wavelength coverage in Å	Intensity performance relative to Mica
LiF-lithium fluoride	420	1.78	down to 0.2	
Topaz	303	2.712	-2.5	4.3
SiO ₂ -quartz	2023	2.75	-2.2	2.8
LiF-lithium fluoride	220	2.848		
LiF*-lithium fluoride	200	4.0267	-3.8	12.8
Al-aluminum	100	4.049	0.8-4.3	20.0
SiO ₂ -quartz	1120	4.903	0.8-4.7	1.4
NaCl-sodium chloride	200	5.640	0.9-5.3	15.1
Calcite	104	6.07	1.0-5.7	4.9
ADP-ammonium dihydrogen phosphate	112	6.14	1.0-5.7	
Si-silicon	111	6.2706		
Fluorite		6.2	1.1-5.8	4.1
Ge-germanium	111	6.532	1.1-6.0	6.6
SiO ₂ *-quartz	1011	6.6862	1.1-6.3	5.3
C-pyrolytic graphite	002	6.70		
ADP-ammonium dihydrogen phosphate	200	7.50	1.2-7.3	
SiO ₂ *-quartz	1010	8.492	1.4-8.1	1.5
PET* pentaerythritol	002	8.74	1.4-8.3	11.8
EDDT-ethylene diamine d-tartrate	020	8.808	1.4-8.3	7.4
ADP*-ammonium dihydrogen phosphate	101	10.642	1.8-10.3	3.5
SHA-sorbitol hexaacetate	110	13.98		
Gypsum	020	15.2	2.6-15.0	1.9
BiTitanate		16.40	-16.0	
Ammonium tartrate		14.2		0.2 ^a
Ammonium citrate		14.7		0.2 ^a
Mica*-muscovite	002	19.84	3.3-19.4	1.0
TLAP-thallium acid phthalate	1010	25.9		
RAP-rubidium acid phthalate		26.121	2.0-18.3	
KAP*-potassium acid phthalate	1010	26.632	4.5-25.4	6.4
Penninite		28.6		0.2
Chlor-clinochlore	0001	28.392	5. -27.4	0.4
Fe-Mg layered ^b		60	8.3-23.7	
OHM-octadecyl hydrogen maleate		63.5		0.4
Llaur-lead laurate		70	-67	15 ^a
LTD ^c -lead tetradeconate		80		
Lmyr-lead myristate		80.5	18-71	
OAD-di-octadecyl adipate		93.8		
OHS-octadecyl hydrogen succinate		96.9		
LSD-lead stearate decanoate		100	17-94	15 ^a
LOD*-lead octadecanoate		100	17-94	10.7
Fe-Mg layered ^d		104		
LTE ^c -lead tetracosanoate		126		
Llign*-lead lignocerate		130	26-120	4 ^a
Lcer-lead cerotate		140	31-124	
LTC ^c -lead triacontanoate		156		
Lmel-lead melissate		160	35-140	

*Indicates the crystals that have been commonly used in electron probe analysis.

a) Relative intensity related to mica at 13.3 Å by Henke and Lent (Ref. 56); b) 130 alternating layers each of Fe(14Å) and Mg(16Å); c) pseudo-crystal produced by Biodynamics Research Corp., Rockville, Maryland; d) 100 alternating layers each of Fe(13Å) and Mg(39Å).

layers (Fe) separated by spacing layers (Mg), represented a unique approach but did not perform as well as LSD in the analysis of oxygen or fluorine [53]. Clinochlore has been thoroughly studied [54, 55] and found to provide considerably better resolution and peak intensity than KAP for the analysis of oxygen (23.7 Å). It has not found widespread use in the EPA because, as shown in Fig. 13, from Whatley [55], the intensity drops to low values at wavelengths below those of oxygen, thus the performance of the crystal is superior only for a limited wavelength range. Clinochlore also gives many strong orders of

diffraction leading to spectral interference problems. The resolution of pyrolytic graphite is insufficient for most applications. PET probably represents the most useful recent addition to available crystals providing excellent performance in the range of about 2 to 7 Å. Lead lignocerate has made possible the analysis of Be in some instruments. The most promising crystal at the present time would appear to be RAP, which Whatley [55] has found (Fig. 13) to be superior to KAP at all wavelengths. The intensity is usually more than twice that of KAP, with comparable resolution and a superior P/B value. We,

unfortunately, tried two RAP crystals with no success, apparently because of crystal imperfections. Quality control in the manufacture of many of the organic crystals is a serious problem. Böhm and Ulmer [57] have recently reported on the performance of OAO and TLAP, the latter providing equivalent resolution and an intensity 3.7 times as great as that of KAP.

Two complete reference tables for use in X-ray emission analysis have recently been published [58]. One [59], useful in WDS, provides 2θ values for all X-ray lines with $\lambda < 160$ Å for 23 of the most common crystals used in the EPA. The other [60],

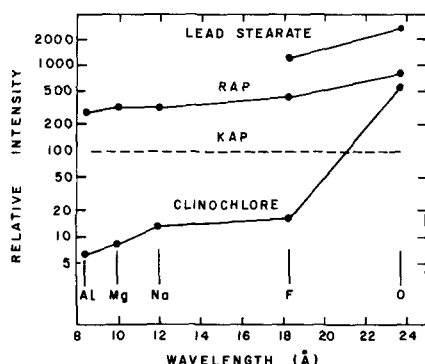


Fig. 13—The relative intensity diffracted by lead stearate, RAP, KAP, and clinocllore crystals in the 8 to 25-Å wavelength region. The work was performed by Whalley [55] using an ARL EPA.

useful in EDS, tabulates the energy of the X-ray lines by element and also arranges the elements according to energy. Both are ASTM publications.

Gratings/ Gratings, like some crystals, have been discussed for some time [61–64] but have not been incorporated into any instruments except on an experimental basis. Some reasons for this are (1) alignment and control of a grating spectrometer can be difficult, for example, with glass the critical angle in degrees is about one tenth of the radiation wavelength in angstroms [61]; (2) the grating spectrometer is different from the crystal spectrometer, necessitating new hardware and eliminating the possibility of interchangeability between crystals and gratings; (3) the grating performance is degraded by contamination; (4) vibration may be a problem; (5) photon collection efficiency has been low; and (6) competitive soap film pseudocrystals can easily be incorporated into existing spec-

trometers and provide fairly good intensities down to Be. No doubt the advent of the soap films delayed the development of grating spectrometers.

In spite of these problems, a grating offers several advantages over a crystal spectrometer: (1) the grating spectrometer is not particularly complex; (2) a wide range of wavelengths can be covered by a single grating; (3) better performance (sensitivity and *P/B* ratio) at long wavelengths can be attained; (4) the analysis of soft X-radiation (up to 250 Å) should be possible; and (5) the good resolution for soft X-rays will be useful in studying the effects of chemical bonding on X-ray emission.

The most exciting and promising recent development was described by Davidson et al [65] at the last national meeting of the Electron Probe Analysis Society of America. They have constructed an automated, blazed grating spectrometer for use on a microprobe. The spectrometer contains a flow proportional detector and a gold coated concave diffraction grating [64] with 1200 grooves per millimeter blazed at a 1-deg angle. The wavelength coverage is 8 to 200 Å, (the limit with the pseudocrystals has been about 160 Å), and the performance compares favorably with crystal spectrometers in the same and other instruments as indicated in Table 6. These results are encouraging and will stimulate further work on the use of grating spectrometers.

Proportional Detectors/ In crystal spectrometers, sealed and thin window flow proportional detectors are now used almost universally and the work has been concentrated on studying the intensity dependent

pulse amplitude [66–70] and detector deadtime [71–74]. Significant improvements in sensitivity have been obtained for some elements by operating flow proportional detectors both above and below atmospheric pressure [75].

All of the activity in the area of gun brightness and detection will undoubtedly lead to another generation of instruments capable of low current, high spatial resolution performance. Such developments will facilitate the analysis of specimens that characteristically provide low emission, such as thin films, liquids, and liquid containing materials. Cosslett [13] has predicted that improvements in brightness and detection could result in the analysis of areas a few hundred angstroms in diameter in transmission specimens.

Energy Dispersive Spectrometers

History and General Description/ High resolution, solid state X-radiation detectors hold great promise and have and will contribute significantly to microanalysis. The widespread use of these devices prompted a one-day technical workshop entirely devoted to energy dispersion X-ray analysis at a recent ASTM meeting in Toronto [76]. Reference will often be made to several fine papers presented at this symposium. Let us begin by briefly discussing what the device consists and is capable of and indicating what uses are current or sought.

What is referred to as an energy dispersive spectrometer (EDS) or energy dispersive X-ray analysis (EDX) has in the past usually been called nondispersive analysis, in contrast to the wavelength

Table 6—Comparative Performance of Diffracting Crystal and Grating Spectrometers

Type of spectrometer		Grating ¹		Grating ¹		Crystal ¹		Crystal ⁵		Crystal ⁷	
EPA Manufacturer		ARL		ARL		ARL		CAMECA		JEOL	
Exit slit in mm		.05		.25		.50					
Analyzed radiation	Wavelength in Å	Peak* and peak/background for each spectrometer									
		P	P/B	P	P/B	P	P/B	P	P/B	P	P/B
FKα	18.3	51	178	190	72	48 ²	500	8.2 ⁶	870	11 ⁸	280
OKα	23.7	34	243	116	70	9.5 ²	500	10.6 ³	110	30 ³	20
CKα	44	35	170	115	105	60 ³	100	19.5 ³	125	40 ³	70
BKα	67							3.8 ³	160	15 ³	50
BeKα	113			2.5	123	4.2 ⁴	200	nd		1.2 ⁹	50
SiLα	123			0.7	42	nd		nd			
AlLα	170			0.06	25	nd		nd		nd	

*P is in 1000 cps at 10 kV and a beam current of 1μa; all intensities normalized to pure element.

1) Davidson et al. (Ref. 65); 2) RAP crystal; 3) LSD crystal; 4) Lignocerate crystal; 5) Beaman; 6) KAP at 20 kV; 7) JEOL (manufacturer's specifications); 8) KAP crystal; 9) Cerotate crystal.

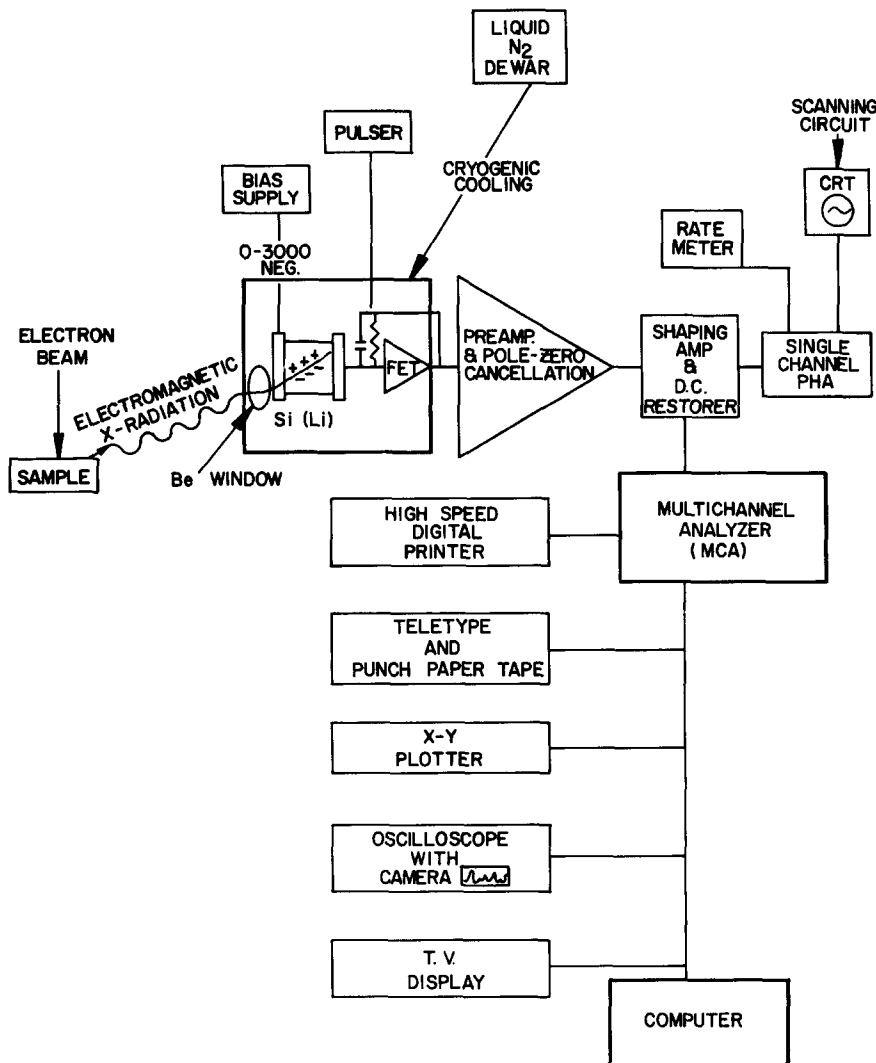


Fig. 14—Schematic drawing of an energy dispersive spectrometer showing the Li drifted Si detector, associated electronics, multichannel analyzer, and several readout capabilities.

dispersive spectrometer (WDS) already discussed and universally used in electron probe analyzers. EDS is becoming the preferred usage. The heart of the EDS is a Li drifted Si semiconductor radiation detector. This detector, with a surface area ranging from about 5 to 200 mm², is located between two metal electrodes across which a bias voltage of about 500 to 900 V is applied. X-rays impinging upon the detector create free charge carriers (electron hole pairs) by photoelectric absorption and subsequent impact ionization. The number of carriers is proportional to the X-ray energy and is given by the ratio of the X-ray energy to the energy required to create a pair (in Si about 3.8 eV at 77 K). The integrated current charge, collected under the influence of the bias at the electrode, is fed to a field effect transistor (FET) in a FET preamplifier as shown in Fig. 14. The high gain, low noise, well grounded FET preamplifier is essential

owing to the lack of amplification in the solid state detector and the resulting low amplitude pulse— $Q(\text{maximum collected charge}) = (E(\text{X-ray})/3.8)(1.6 \times 10^{-19})$ C. The output voltage pulse from the preamplifier is further amplified and shaped in a linear amplifier with variable time constants and passed to a multichannel analyzer (MCA). In the MCA the voltage pulses are separated on the basis of amplitude and stored in the memory channel corresponding to a particular energy increment. The resulting spectrum can be displayed on a CRT or *xy* strip chart recorder, printed out by a high speed printer, placed on punch paper tape, or transferred directly to a computer. In Fig. 15 the energy spectrum from a commercial alloy is shown as it appeared on a CRT.

The EDS has created a flurry of activity because it can be easily added to a scanning electron microscope (SEM) and pos-

sesses sufficient sensitivity to provide X-ray data at beam currents well below those encountered in the electron probe, namely, those typically used in a SEM. Thus, the possibility of obtaining chemical information using an SEM with high resolution (100 to 250 Å) and good imaging capabilities does exist; however, this does not mean that chemical concentrations can be determined for specimen constituents of this size, since the electron scattering discussed earlier is still the predominant factor in determining spatial resolution.

An important decision facing prospective instrument purchasers is whether to select an EPA equipped with SEM capabilities (a secondary electron detection system) or a SEM with analytical capabilities (EDS). It is obvious that the decision will depend to a great extent upon the type of problems anticipated, the work load, and the funds available; nevertheless, the inherent features of the SEM-EDS and EPA-WDS combinations will play a major role in that decision. Let us now pursue in some detail the advantages and disadvantages of the EDS in a climate free from the enthusiasm, exuberance, and consequent exaggeration that naturally surrounds a promising new development marketed by a number of manufacturers.

Advantages and Performance/ It is misleading to say that EDS is new. What should be said is that high resolution EDS is new (S is used in EDS interchangeably to mean spectrometer or spectrometry). The resolution of an EDS is usually taken to be the total energy spread in a particular X-ray line at one-half maximum intensity (FWHM) measured after the accumulation of a large number of counts at a low total spectrum counting rate. The typical FWHM of the Mn K α peak at 5.9 keV will be between 160 to 200 eV for a 6-mm² detector at a total spectrum counting rate of 1000 cps and an accumulated count in the Mn peak of over 100,000 counts.

Birks and Batt [78] described in 1963

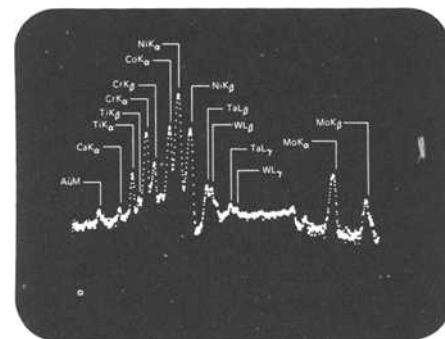


Fig. 15—A typical energy spectrum from an EDS as displayed on a cathode ray tube. The system resolution is about 180 eV at 5.9 keV and the specimen is a commercial superalloy. Courtesy of Albrecht [77].

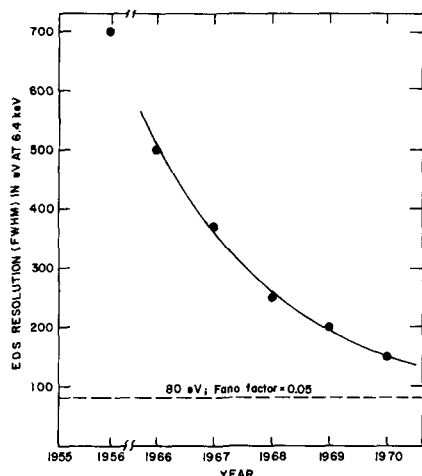


Fig. 16—The resolution race in energy dispersive spectrometers. The resolution at 6.4 keV (Fe $K\alpha$) is shown as a function of year. Information provided by Gedcke [81].

the use of a sealed proportional counter with a 400-channel MCA on an electron microprobe. The resolution represented by the full width at half maximum (FWHM) intensity was over 1000 eV at 6.4 keV (Fe $K\alpha$) and the Cr, Fe, and Ni X-ray peaks overlapped significantly; however, they were able to mathematically unfold (deconvolute) the spectrum with good success using the Dolby method [79]. Dolby [79,80] discussed the deconvolution of the energy spectra obtained using a gas proportional detector, and in 1963 [80] used it to obtain scanning images of Be, C, and O. The original Cambridge EPAs available in 1959 were equipped with proportional detectors that could be used in an EDS mode. The EDS of Birks and Batt [78] did not become widely used primarily due to the inadequate resolution and the need for extensive deconvolution at a time when computers were not as readily accessible as they are now.

What has occurred in the resolution race is most remarkable, as indicated in Fig. 16 [81]. Some recently advertised resolution values (FWHM) in electron volts for those elements indicated in parentheses are 109 (Al $K\alpha$), 125 (Si $K\alpha$), 153 (Mn $K\alpha$), 197 (Pt $L\alpha_1$), 238 (Np $L\alpha_1$), 85 (pulser), and 160 (Fe $K\alpha$). In a recently delivered system, a resolution of 157 eV (Fe $K\alpha$) with a 28-mm² detector has been achieved. At the time of writing, the best reported resolution was about 145 eV for Mn $K\alpha$. As will be shown later, the FWHM resolution in a particular system increases with the square root of the X-ray line energy.

Resolution of the EDS is important because it is indicative of a system's ability to resolve peaks of neighboring elements, and the better the resolution the fewer the energy interferences that will be encountered and the less sophistication required

in the deconvolution techniques. The need for high resolution is indicated in Fig. 17, where the X-ray energy is plotted against the atomic number for various X-ray lines. Charts and tables [60] are available from which possible energy interferences can readily be identified. It is evident from the width of the indicated energy bands in Fig. 17 that the number of possible interferences increases rapidly with diminished resolution, for example, at Si $K\alpha$ the number of possible interferences increases from 12 to 24 when the encompassed energy interval increases from ± 200 eV to ± 400 eV. The present state of the art is such that $K\alpha$ lines of adjacent elements can readily be resolved when the elements are present in about equal amounts and $Z > 10$.

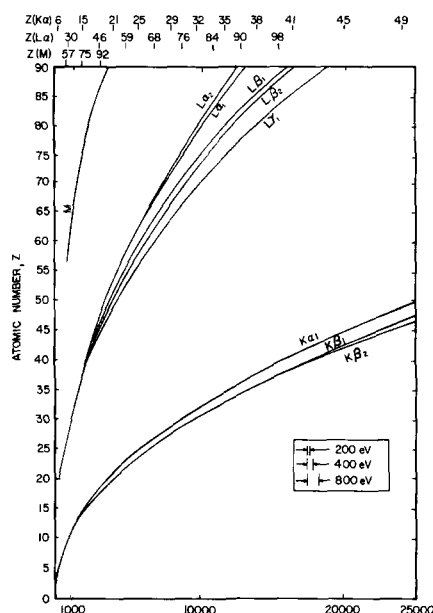


Fig. 17—K, L, and M X-ray emission energies as a function of atomic number. The atomic number ranges corresponding to various $K\alpha$, $L\alpha$, and M energy ranges are shown on the top portion of the graph. Energy bands of 200, 400, and 800 eV are drawn to illustrate possible energy interferences.

Fitzgerald and Gantzel [82] have appropriately pointed out that, in EDS systems, overlapping peaks are the rule and not the exception. For a gaussian distribution the full width tenth maximum (FWTM), is 1.83 FWHM, or 366 eV for a detector with a resolution of 200 eV. The resolution at FWTM is of significance, because it is indicative of the system's ability to resolve peaks when the concentration is low and is directly related to the peak to background ratio (P/B), which in turn affects the detectability limit. It should be noted that universal agreement has not yet been reached on how to measure and quote resolution values, since for

a given detector they depend upon many factors, such as the peak height selected for measuring resolution, that is, FWHM or FWHM above background or FWTM; the number of counts collected in the peak channel; the energy of the line; the overall spectrum counting rate; the amplifier time constant; and the base line restoration.

The question of resolution arises because monoenergetic photons do not produce pulses with a fixed energy. Since the generation of charge carriers in the detector is statistical in nature, there is an energy distribution of generated pulses with a standard deviation σ about a mean energy which is proportional to the energy of the X-ray photon. When ϵ is the average energy required to produce an electron-hole pair (3.8 eV at 77 K in Si), E is the energy of the X-ray photon, and F is the Fano factor, the standard deviation is given by $\sigma = \sqrt{E\epsilon F}$. F is the ratio of the variance of an actual distribution to that given by a Poisson distribution and has been found to be well below unity, indicating considerably less fluctuation than predicted by Poisson statistics. Experimental measurements indicate an F value of 0.12 to 0.13.

Since in a normal distribution the $\text{FWHM} = 2.35\sigma$, the detector resolution, E_{Si} , can be written as $E_{\text{Si}} = 2.35 \sqrt{E\epsilon F} = 1.65 \sqrt{E}$ where $\epsilon = 3.8$ eV and $F = 0.13$.

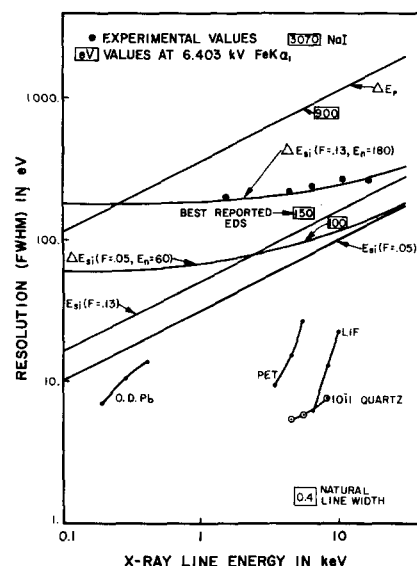


Fig. 18—The resolution of different detectors and spectrometers as a function of X-ray line energy. E_{Si} is the resolution of a Li drifted Si detector; ΔE_{Si} is the resolution of an EDS equipped with a Si detector; ΔE_p is the resolution of an EDS equipped with a gas proportional detector; F is the Fano factor; and E_n is the electronic noise. The closed circles are experimental values, as opposed to the curves which are calculated. The [eV] represents resolution values for the indicated spectrometers and crystals at 6.403 keV (Fe $K\alpha$). The lowest four curves represent the experimentally determined resolution for four wavelength dispersive spectrometers using the indicated crystals.

The resolution of the system is degraded from E_{Si} because of electronic noise, E_n , which arises primarily in the preamplifier. The contribution from detector leakage current (below 10 eV) is small. Other factors that degrade the resolution will be discussed later. A system's E_n is easily measured by using the signal from a pulse generator as the input to the FET preamplifier. The theoretical resolution of an EDS is defined as

$$\Delta E_{Si} \equiv \sqrt{E_{Si}^2 + E_n^2} \text{ at FWHM}$$

The theoretical EDS system resolution, when a flow proportional detector of high internal gain is used, is given by

$$\Delta E_p = E_p = 2.35 \sqrt{E\epsilon} = 11.4 \sqrt{E} \text{ at FWHM}$$

where $F = 1$ and $\epsilon = 26.3$ eV per ion for argon [82]. The percentage resolution is given by ΔE (FWHM) $\times 100/E$.

The dependence of the resolution on photon energy for the different systems shown in Fig. 18 points up several facts. (1) The solid state detector exhibits better resolution than a gas proportional detector for energies above 250 eV ($Z > 5$). A value of 180 for E_n was used, because at the time the measurements were made our own system exhibited this noise level. Typical values for E_n in systems now available range from 80 to 100 eV. (2) At low energies E_n predominates whereas at high energies E_{Si} predominates in determining ΔE_{Si} . (3) WDSs are capable of much better resolution than EDSs except at high energies ($E > 20$ keV). (4) The predicted limit on resolution at 6.4 keV (Fe $K\alpha$) with an EDS is about 100 eV based on $F = 0.05$ and $E_n = 60$ eV. An experimental F value of 0.075 has been reported [83]. Considering the rate of improvement in resolution indicated in Fig. 16 and the present estimates of theoretical limits, it appears that delaying the purchase of an EDS on the basis of expected resolution gains is probably not advisable, particularly as future improvements in resolution will certainly be costly.

Perhaps the most outstanding feature of an EDS is the short period of time in which an analysis can be performed. The entire X-ray spectrum from 0.1 to about 12 Å is obtained easily in a matter of 0.5 to 5 min at modest concentration levels. In an EPA with a WDS much longer times are required when scanning the entire spectrum, because the WDS spends only a minute portion of the total spectral scanning time at any particular wavelength while the EDS accumulates counts continuously at all energies. The use of programmed or computer controlled spectrometers has made scanning with a WDS considerably more efficient than but still not competitive with an EDS. The EDS requires only

Table 7—Performance Data for Wavelength and Energy Dispersive Spectrometers in Electron Probes and Scanning Electron Microscopes

Investigator	Reference No.	Type of Instrument	Manufacturer	EDS or WDS	EDS manufacturer	Crystal diameter(mm)	Crystal area(mm ²)	Source to crystal(mm)	Solid angle(10 ⁻⁴ sterad)	f range	f range in ev	Beam current(na)	E ₀ (kv)	Take-off angle(°)	Acquire time(sec)	Be window(.001")	Integrated (J) or peak (P) counts per second per nanoampere and peak/background (P/B) ratio																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																									
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Lifshin	85	EPA	CAMECA	EDS	Ortec	4	3.1	12.5	270	0.4	complete	FWHM	315	5	20	52.5	2	2	20	20	50 ^b	43	100	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

a) 4mm crystal collimated to 2mm; b) except 40kV on Al; c) adjusted to account for difference in solid angle and f range so data refers to a 4mm crystal and f FWHM; d) 30kV.

one detector, whereas in most EPAs there are a multiplicity of spectrometers and crystals. To cover the range from 0.8 to 44 Å with optimum sensitivity for all elements in our probe would involve four spectrometers, which would have to be scanning simultaneously, LSD, KAP, PET, 10 $\bar{1}$ 1 quartz, and LiF crystals, and a typical spectral scan period of about 1 h. Woodhouse [84] reported that on his probe a complete spectral scan required 26 min. In an EPA the ideal situation is to use the EDS in a preliminary investigation to determine the elements present and then to make accurate measurements and solve energy interference difficulties with the WDS. There is no doubt that the use of an EDS greatly facilitates the analysis of probe specimens particularly when starting with little or no knowledge of their chemistry.

EDS provides this rapid analytical capability as a result of an extremely high sensitivity, which is defined as the measured intensity per unit beam current (cps/nA = counts per second per nanoampere). As will be shown, the EDS can often have sensitivities of over 10,000 cps/nA, whereas 1000 cps/nA is high for a WDS. The high sensitivity is the result of three characteristics, namely, large solid angle, detection without diffraction, and high detector efficiency. Because the EDS lacks diffracting crystals and any mechanical motion, the detector and detector housing are small and can be placed in close proximity to the specimen, thereby subtending a large solid angle. As Table 7 shows, solid angles in the range of 10 to 40 $\times 10^{-4}$ sr are common in EDS (newer SEM installations have values approaching 10 $^{-2}$ sr), while 1 $\times 10^{-4}$ sr is typical of a WDS in an EPA. The measured intensity is directly proportional to the solid angle.

The absence of a diffracting crystal, in addition to simplifying the geometry, greatly enhances the efficiency of the EDS compared with that of the WDS as diffraction efficiencies are low (<25 percent). The detector itself is highly efficient, e.g., with a 0.001-in. Be window the detector is 100 percent efficient for radiation between 0.7 and 2 Å and over 90 percent efficient for radiation between 0.6 and 4 Å. The efficiencies drop off at longer wavelengths as a result of X-ray absorption in the Be window and at shorter wavelengths because high energy X-rays are able to penetrate the active depth of the detector (typically 3 mm). Flow proportional detectors typically have efficiencies increasing continuously from about 10 percent at 1 Å to 90 percent at 3.8 Å, the excitation energy for argon.

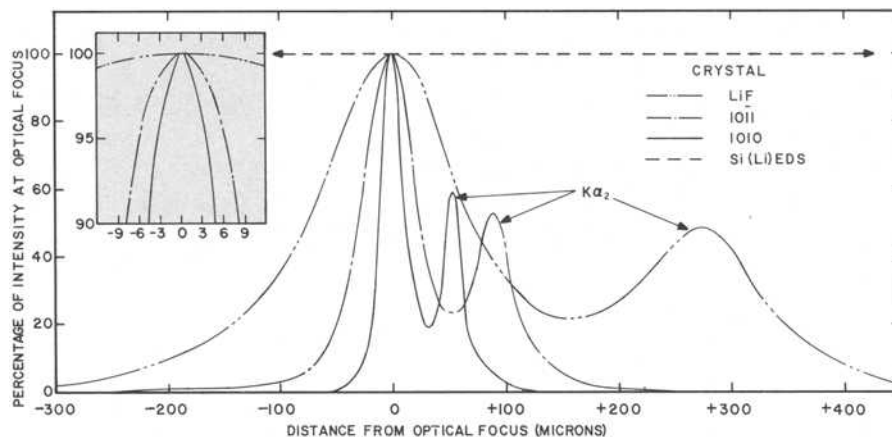


Fig. 19—The dependence of X-ray peak intensity on specimen height. The values are experimental and were measured in an EPA operated at 25 kV. The percentage of the Cu K α_1 intensity emitted by pure Cu at optical focus is plotted as a function of the distance on either side of optical focus. Four spectrometers were studied: an EDS, two WDSs with high resolution (1010) and (1011) quartz crystals, and a WDS with a LiF crystal.

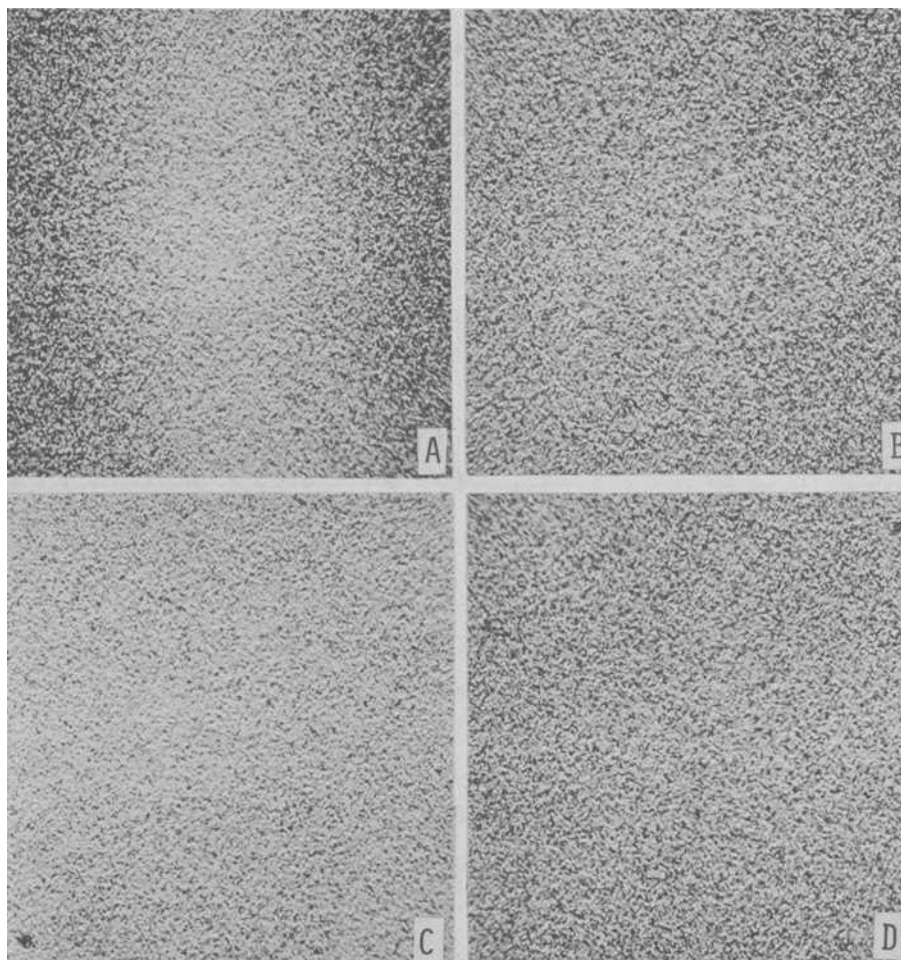


Fig. 20—Defocusing effects in an electron probe analyzer. The electron beam was scanned over a 300 by 300- μ m raster on a highly polished flat and pure Cu specimen at 25 kV: (A) fully electronic scanning with a (1011) quartz crystal WDS; (B) fully electronic scanning with a LiF crystal WDS; (C) electromechanical scanning with a (1011) quartz crystal WDS; (D) fully electronic scanning with an EDS. The loss of focus, is indicated by the darkening at the edges of the photograph.

Table 8—The Advantages of an Energy Dispersive Spectrometer

<u>Outstanding detector resolution</u>
150 eV with a Si(Li) detector
900 eV with a proportional detector
<u>Rapid analysis (minutes)</u>
<u>High sensitivity (10000 cps/nanoampere)</u>
high solid angle (.004 steradian).
no diffraction.
high detector efficiency (100%).
<u>Low current operation (10^{-11} amperes)</u>
no thermal damage.
diffusion minimized.
<u>No x-ray focusing required</u>
lack of sensitivity to specimen height.
no defocusing effects on scanning.
makes completely automated operation feasible.
<u>No diffraction interferences from high order x-ray lines</u>
<u>Simple mechanical design</u>
no moving parts.
easily maintained.
easily added to existing instruments.
<u>Output is compatible with computer</u>
<u>Escape peaks are absent in conventional analysis</u>
<u>Gains in spatial resolution possible in selected cases</u>

In Table 7 the experimentally measured sensitivities for several elements are listed and the difference between EPA-EDS, SEM-EDS, and EPA-WDS combinations are illustrated. The data reveal several interesting features. (1) In the SEM-EDS arrangement high sensitivities are possible and are generally in the range of 1000 to 10,000 cps/nA. (2) In the EPA-EDS combination the sensitivities of 100 to 400 cps/nA are well below those of the SEM-EDS because of the reduced solid angle in the EPA. This small solid angle results from the fact that it is not possible to get the Si detector as close to the specimen in the EPA as in the SEM because of the complexity encountered in the vicinity of the objective lens. The short, fixed working distance (3 mm—to minimize spherical aberration), the presence of coaxial electron and light optical systems, and the need for X-ray spectrometer exit ports, backscattered and secondary electron detectors, anticontamination devices, and controlled oxygen leaks, all contribute to that complexity. EPA users must be aware of this problem and cannot generally expect the marvelous sensitivities presently

possible with SEMs. Another facet of this problem facing EPA users is that some existing instruments do not operate well at low currents; so, in order to use an EDS, currents of 5 to 10 nA are essential. The problem then becomes one of reducing the solid angle so that the counting rates encountered do not degrade EDS performance. (3) The EPA-WDS and SEM-WDS sensitivities are better than that of the EPA-EDS combination. (4) The EDS P/B ratios are commonly one order of magnitude lower than those encountered with a WDS.

High sensitivity provides some substantial benefits. As the sensitivity improves, the same counting levels can be attained at lower beam currents. This is of particular value in the analysis of heat sensitive materials such as soft tissues and blood, and it may make feasible the analysis of diffusible ions (Na, K) in such materials. Low current operation combined with rapid analytical speed helps to alleviate some of the difficulties encountered in the analysis of glass [89–92] where pronounced migration (loss and gain) of Na and K have been reported. As will be shown later, the

higher the sensitivity the lower the limit of detection. The rapid analytical capability minimizes the problems associated with instrumental drift.

There are several secondary advantages besides the primary ones of high sensitivity, rapid total spectrum display, and good detector resolution that are responsible for the EDS's popularity. A historical problem in the EPA has been that of maintaining the spectrometer and light optics in simultaneous focus; a necessity because, for optimum efficiency in a WDS, it is essential that the X-ray source, crystal, and detector lie on the focusing (Rowland) circle. The variation of intensity with specimen height or the deviation from optical focus in a WDS depends upon the spectrometer design, the crystal being used, and the Bragg angle as shown in Fig. 19. The absence of focusing and diffraction phenomena in the EDS alleviates this problem and is, in special cases, of substantial utility.

The National Bureau of Standards [93] utilizes this feature of the EDS in the determination of specimen homogeneity. Because the beam can be moved over large distances without intensity loss, the instrument can be left unattended over night and the data can be automatically collected. In EPAs, where fully electronic beam scanning is used, there can be serious X-ray defocusing when the beam is deflected the usual distances encountered in electron beam scanning, namely 50 to 300 μm , and a diminution of intensity at the extremities of the scan will appear. The loss of focus in many EPAs becomes evident in scanning at deflections of about 100 μm . The problem does not exist in EPAs, where the electron beam is electrostatically deflected in a direction normal to the focusing circle (y direction) while the specimen is rapidly moved beneath the beam tangent to the focusing circle (x direction). Figure 20 illustrates these effects.

The lack of focusing sensitivity is extremely important in the analysis of irregular specimens in the SEM; nonetheless, the user must also be aware of the fact that, as the X-ray source height varies, the X-ray take-off angle and solid angle do undergo small changes. The energy spectrum of an EDS lacks the complication of multiple diffraction orders. A second-order $Y K\alpha$ line ($n\lambda = 1.6604 \text{ \AA}$) would represent a serious diffraction interference problem in the analysis of Ni ($n\lambda = 1.6590 \text{ \AA}$), with a WDS which could only be eliminated by using energy discrimination (pulse height selection).

An EDS is certainly a simple mechanical device in comparison to a WDS. With an

EDS there are no moving parts, no need for complex geometrical configurations with stringent reproducibility requirements (most EPAs have $\pm 0.0001\text{-}\text{\AA}$ spectral reproducibility), no drive screws, gears, or belts to maintain, no crystals to align and realign, no detector windows to break and replace, and no detector anodes to become contaminated. An EDS can be easily added to existing instruments, and one would expect that any future-generation EPA would include an EDS with a large solid angle, making possible the attainment of the sensitivities presently reported for SEMs. The variation of crystal spacing with temperature and the variation of detector efficiency with pressure encountered in a WDS are absent in an EDS.

The advantages of an EDS as compared to a WDS are summarized in Table 8. To this point the EDS has been presented as a panacea for many problems, but unfortunately there are some limitations. Notwithstanding these, the reader should keep in mind that the addition of an EDS to an SEM provides the latter instrument with an analytical capability and that represents a major scientific advancement.

Disadvantages/ The Si detector and FET transistor must be maintained at cryogenic temperatures to reduce thermal noise for an optimum signal to noise ratio and to prevent the drift of Li under the applied bias. The detector can be warmed up if no bias is applied. We are aware of several incidents in which detectors raised to room temperature have shown no degradation in resolution, and one manufacturer [94] guarantees no degradation in resolution after 25 cycles between 77 and 293 K. An important factor here is the length of time at ambient temperature.

The cryogenic requirement leads to several difficulties, the least of which is the nuisance of having to keep a cryostat filled. Considerable ingenuity has reduced the cryostat size but they are still rather bulky, for example, our 5-liter cryostat will run for about five days without refilling and occupies $1/2\text{ ft}^3$. The most important disadvantage of cryostatic operation is the bulk and complexity it adds to the system; it is this problem which makes it difficult to visualize the use of the Si detector in place of the proportional detectors found in the WDS. The bulk, in addition to the cold detector surface, makes the placement of the detector, without isolation, inside the chamber of an EPA or SEM a complex process. Elad [95] reports that the bubbling of the liquid nitrogen in the cryostat creates microphonics that can degrade resolution.

In all present installations the Si detector is maintained under static vacuum in

a housing which is isolated from the electron beam instrument by a thin Be window. The Be is needed for several reasons: (1) since the crystal is necessarily cold, it would act as a trap and become contaminated by water vapor and pump oils in the dynamic vacuums found in most existing EPAs and SEMs (10^{-5} torr); (2) the detector is light sensitive; (3) backscattered electrons are absorbed by the Be; and (4) it serves as a vacuum seal between the EDS and the instrument column.

The disadvantage of the Be is that it absorbs long wavelength radiation, thus restricting present analysis to atomic numbers above ten. To lower this limit, interest has developed in the thin plastic windows (collodian, Formvar) used extensively in EPAs as flow proportional detector windows and as isolation barriers between the electron column and the WDS. Any plastic window will have to be opaque (metal coating), supported (wire grid), and probably equipped with a vacuum interlock and valve to be activated upon window failure. A magnetic trap for backscattered electrons will also be necessary. The complete assembly could easily cost more than the detector. A large amount of effort has been diverted from the development of long wavelength EDS because of the low energy noise levels of existing systems and the serious energy interferences encountered below 1 keV (discussed later). Beryllium windows of less than 0.001 in. in thickness have been tried and some manufacturers supply 0.0005 and 0.0003-in. sheets. At lower thickness pinholes may develop and window fragility becomes a problem. Figure 21 illustrates the improvement in X-ray transmission obtainable from thin Be or plastic windows.

Both flow proportional detectors and EDSs exhibit intensity sensitivity. In a flow proportional detector the pulse amplitude diminishes with increasing intensity and pulses may be lost as a result of clipping by the PHA base line [66-68]. Spielberg [68-70] has thoroughly pursued this problem and found that the effect can be substantially reduced by maintaining a clean anode wire. Lifshin [96] and Beaman et al [97] confirm this. The intensity sensitivity encountered in an EDS refers to a degraded resolution (and therefore P/B) with increasing total spectrum counting rates above 10,000 cps, primarily due to pulse pile-up. Long amplifier time constants (8 μs) and d-c restoration give optimum resolution at low intensities but degrade the resolution at higher intensities, while short amplifier time constants (2 μs) and no (or passive) d-c restoration give inferior resolution at low counting rates but retain the resolution to higher intensities (40,000 cps).

The usual procedure is to operate with the longer time constant to obtain maximum resolution and use a low enough current to avoid the line broadening due to pulse pile-up. If high intensities cannot be avoided (high current probe, low concentration of an element of interest), resolution must usually be sacrificed through the use of a short time constant to maintain constant resolution. Improvements in this area should be forthcoming. A variation of line width with intensity could be troublesome if a computer program were used to mathematically unfold the energy spectrum. Even at lower intensities there is often a slight variation of line width with intensity. Landis et al [98] have developed preamplifiers using pulsed-light electronic feedback which will rectify this problem; however, electronic deadtime problems need to be accounted for as the counting rate increases.

The escape peaks [99] encountered when using gas proportional counters are generally considered to be absent with a Si detector. In a proportional detector the energy of the escape peak is the difference between the energy of the incoming photon and the energy of the $K\alpha_1$ gas photon, usually argon. The generated photon escapes detection because of the low efficiency of the detector for that wavelength. Woodhouse [84] has reported on an escape phenomena when using Si detectors. Using a ^{57}Co source and an EDS, counts were accumulated for 50,000 s and a peak was observed whose energy was 1740 V less than that of Fe $K\alpha$, which corresponds to a Si escape peak— $E_c(\text{Si } K\alpha) = 1.740\text{ keV}$. Woodhouse proposed that this was due to excitation of Si $K\alpha$ radiation at the crystal (Li drifted Si) surface.

If an EDS is to be used on a routine basis for quantitative analysis in systems containing more than two elements, computer reduction of the accumulated spectra is essential because of the relatively poor spectral resolution and the low P/B ratios. From an experimental spectrum a computer program must extract peak location, that is, elemental identification; peak magnitude, P ; and background magnitude, B . The program should calculate $P - B$ corrected for counting losses; the ratio $k = (P' - B')/(P^0 - B^0)$, where the prime and zero refer to the unknown and standard materials, respectively; and, finally, the concentration using one of the EPA quantitative correction programs. There are programs available for deconvoluting and smoothing experimental spectra [100-103] which need to be adapted to the problems encountered in EDX.

A major problem is the accurate deter-

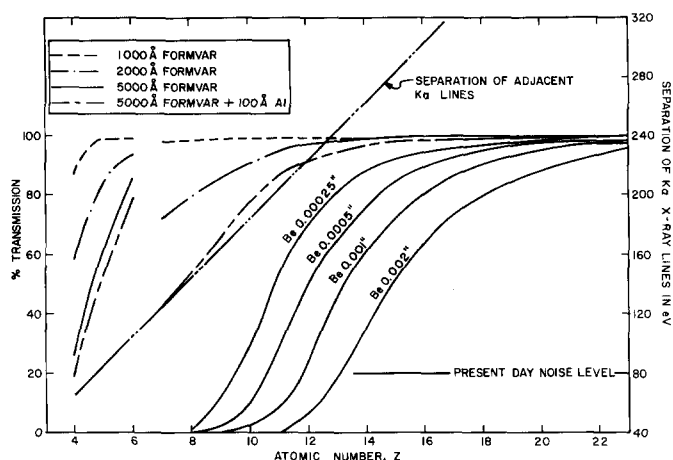
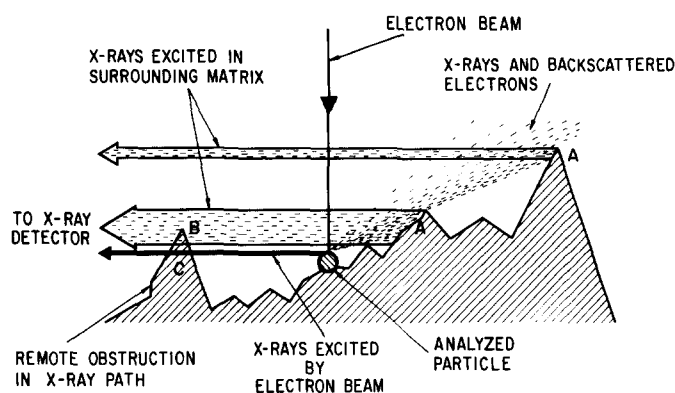


Fig. 21—The percent intensity transmission of $K\alpha$ X-ray lines through various thin windows as a function of the atomic number of the emitter. Curves are drawn for unsupported Formvar films, Formvar films with a 100-Å coating of Al, and four different thicknesses of Be. The right-hand axis is used to plot the energy separation of



adjacent $K\alpha$ X-ray lines as a function of atomic number. (left)

Fig. 22—A schematic diagram illustrating some difficulties that can be encountered in the analysis of rough specimens with energy dispersive spectrometers. At points A, X-radiation is generated by primary X-radiation and also by backscattered electrons emitted by the analyzed particle. At points B and C, absorption of the generated X-radiation takes place. Photograph courtesy of Bomback [49]. (above)

mination of the background in a spectrum where the background constitutes a significant portion of the peak and does not vary continuously with energy. For example, Lifshin [104] reported a P/B ratio of 30/1 on the low energy side of an Fe $K\alpha$ peak and a P/B ratio of 50/1 on the high energy side. As will be shown later this problem becomes more serious as the concentration decreases. While no specific program is available for distribution at this time, several laboratories are working on the problem [82, 105–107].

The first attempt at quantitative analysis with an EDS was performed by Birks and Batt in 1963 [78]. Their composition values obtained with the EDS and WDS differed by less than 0.8 absolute weight percent. They simply subtracted a background value, estimated from the alloy spectrum, from the peak intensity in the channel corresponding to the pure element. This measured intensity in the alloy, I_i , was then equated to

$$I_i' = I_{ii}^0 k_i + \sum_{j=2}^n I_{ij}^0 k_j \frac{I_{ji}^0}{I_{jj}^0}$$

$$= I_{ii}^0 k_i + \sum_{j=2}^n k_j I_{ji}^0$$

where k is the X-ray intensity ratio (alloy/pure). The first subscript indicates the target element and the second subscript indicates the element representing the energy channel where the contribution from the first subscripted element is to be measured; for example, I_{BA}^0 is the intensity from a pure B target in the energy channel corresponding to an A X-ray line. The n represents the number of components and, thus, the number of equations.

The two most serious disadvantages of an EDS are its present limitations in quantitative analysis (to be discussed) and its sensitivity to all generated X-ray signals regardless of source. Bomback [49] presented an outstanding paper at the Toronto ASTM meeting which, while serving as a tempering influence on the use of EDS, will actually promote its use by providing useful guidelines to help avoid some serious mistakes that, once made, could severely limit the widespread use of the technique.

Figure 22, taken from his paper, indicates several difficulties in the analysis of small particles on or in an irregular surface. Backscattered primary electrons can excite radiation in remote parts of the specimen (area A) that will be detected by the EDS due to the fact that the EDS is insensitive to source position and thus does not discriminate against stray X-radiation. These backscattered electrons can also excite characteristic X-radiation in instrument components such as the objective pole piece, the magnetic traps, and the anti-contamination devices. The X-radiation emitted by the particle can cause secondary X-ray fluorescence (areas A and B). The radiation emitted by the particle can be absorbed by surface irregularities, reducing the emitted intensity (as at area C). Bomback placed a 0.02-in. Ni wire on a Th substrate and measured 12 percent Ni when the location of the beam was 10 μm from the wire. When the beam was 1000 μm from the wire he still measured 2 percent Ni. In a MnS inclusion (diameter of about 9 μm) on a steel fracture surface Bomback measured S/Mn intensity ratios varying from 0.2 to 1.25 as a result of different absorption paths in the inclusion itself. Such topographic effects can also be misleading in electron beam scanning

when the EDS is set for a particular energy interval.

The Bomback paper stresses the need for taking background scans by photographing the same area with the analyzer set for an adjacent energy interval in which only continuous radiation contributes to the signal. Equal exposure times can be used to determine whether there actually is a signal above the background noise and equal count exposures can be used to detect topographic contrast. There are some photographs in the Bomback paper that dramatically illustrate these effects and will certainly serve as a sobering influence on anyone intoxicated with the vast potential of EDS. The stringent focusing requirements of a WDS (X-ray source on the focusing circle) can often be utilized to good advantage.

Analytical Considerations in EDX/ The advantages and disadvantages of an EDS just discussed, affect the actual performance of these systems in four specific areas: (1) the accuracy and precision of quantitative analysis, (2) the detectability limits, $C(LD)$, (3) the spatial resolution, and (4) long wavelength or light element analysis.

Analysis of Light Elements—Considering first the extension of the analytical capabilities of the EDS to include long wavelength radiation is just as interesting and important now as it was several years ago when EPAs were restricted to the analysis of elements with $Z > 10$. Fluorine is important in dental research; carbon, nitrogen, and oxygen are of great interest in biology and metallurgy; oxygen is involved in most mineralogical investigations; Be and B are commonly encountered in metals and ceramics research. The only reported light element analysis with an EDS is that of Elad et al [108], who

Table 9—Summary of Quantitative Analyses Performed Using Energy Dispersive Spectrometers

[illegible]

1) $\Delta k/k = \{k(\text{expt}) - k(\text{calc})\} / k(\text{calc})$; 2) $\Delta C/C = \{C(\text{expt}) - C(\text{true})\} / C(\text{true})$; 3) 35 kV.

were able to detect oxygen in SiO₂ using a Be window that presumably contained pinholes [109]. Russ [107] mentions some unpublished work of Jaklevic and Goulding in which carbon was detected using an EDS. The use of plastic isolation windows will remove the physical limitation caused by absorption in the Be window. Russ [107] also discussed the use of window-less systems in ultrahigh vacuum instruments.

Once the absorption problem is overcome there would appear to be three approaches to light element analyses: (1) use of an EDS equipped with both a solid state and flow proportional counter connected either in tandem [110] or with a switching arrangement; (2) if there is sufficient room, use of both an EDS and a WDS; or (3) use of Si detectors with improved resolution. An important consideration in the analysis of long wavelengths with an EDS is that of energy interference. One is seldom interested in the analysis of a light element in the absence of heavier ones, and there are a multitude of interfering L and M lines for X-ray energies below 1 keV. Sutfin [111] has pointed out that within 100 eV of the C K α line (283 eV) there are 87 X-ray lines, most of which represent common elements (see Fig. 17), while within 200 eV of the Fe K α line there are 29 X-ray lines, only two of which represent a common element (Mn and Fe).

The electronic noise peak at zero energy is also a limitation in the analysis of low energy peaks. The minimum energy that could be accurately analyzed is the sum of the total width of the noise peak above zero energy plus one half of the FWTM of the pulser noise peak. In our own system, with a pulser noise peak of 180 eV (FWHM at 2 keV), the noise peak at zero energy drops to a background level at 360 eV (FWTM = 300 eV) and the minimum energy that could be analyzed would be 525 eV (360 + 1.83 (180/2)), which is about 2.4 times as large as our system's resolution of 220 eV (FWHM at 6.4 keV). With the best systems available today the limit is about 250 eV, allowing in theory the analysis of all elements with $Z > 6$.

The energy separation of K α lines decreases from 190 eV at $Z = 10$ to 75 eV at $Z = 4$ and the separation between C and N is only 110 eV as shown in Fig. 21. To obtain good separation of C and N would require a FWHM of 60 eV and systems of considerably lower noise level than those presently available; however, in most applications, neighboring light elements do not occur. At low energy levels, problems previously neglected may develop within the detector that will require attention (nonlinear charge collection, increased trapping). Because of the multitude of possible low energy interferences, the insufficient resolution of ei-

Table 10—The Percentage of Relative Errors in Seven Investigations within the Indicated Limits

Principal author	No. of analyses	Method of analysis ¹	Percentage of analyses within indicated %						
			+1	+2	+4	+6	+10	+20	+40
Beaman	12	f	17	42	58	83	100		
Myklebust	32	f	22	47	59	69	84	97	100
Above 2	44	f	20	45	59	73	89	98	100
Lifshin	14	f	8	8	36	36	71	86	93
Tenny	15		33	33	33	47	60	73	80
Above 4 (C>19%)	59		19	37	53	66	86	98	100
Russ (adjusted)	6	f	50	50	67	67	84	100	
Russ	64	f		72					
Beaman	16	P-B	25	44	69	82	100		
Myklebust	16	P-B	19	31	50	56	81	88	100
The results below were obtained with a WDS on an EPA.									
Beaman	12	P-B	75	100					
Duncumb	333	P-B	45	60	80	87	93	99	
Heinrich	109	P-B	32	64	88	98	100		

1) f means integrated intensities are used in calculating k; P-B means k is obtained from the difference between the spectral peak and spectral background intensities.

ther Si or flow proportional detectors, the low energy noise, the close proximity of K α X-ray lines at low Z, and the catastrophic consequences (probable detector destruction) of thin window failure when using a Si detector, the use of a WDS for light element analysis is recommended.

A combination WDS-EDS instrument, of course, overcomes the many difficulties previously discussed with an EDS. Several manufacturers have recently announced the availability of WDSs for their SEMs. Generally, they are expensive and designed to cover the complete spectral range. There is no reason why a less expensive spectrometer could not be designed for analyzing light elements only; however, the more expensive apparatus (multispectrometer, multicrystal, multidetector, multicounting channels) provides high resolution where needed, detects the signal from a single X-ray source only, offers a known quantitative capability, and gives complete spectral coverage (Be to U). These gains are certainly well worth the extra cost. Indiscriminate addition of a WDS to existing SEMs must be avoided because some cannot be operated at sufficiently high currents (1 to 100-nA range) to make use of a low sensitivity WDS. Fortunately, the newer instruments do have broad ranges of current capability. More will be said later concerning the conversion of an SEM into an EPA.

Accuracy—The experimental accuracy and precision attainable in the determination of an X-ray intensity ratio, k , using an EDS with a Si detector have not yet been firmly established, regardless of any

claims to the contrary. Attempts at quantitative analysis have been made by: Russ [86], Beaman and Solosky (reported herein), Myklebust and Heinrich [106, 112], Heinrich [110], Lifshin [96], Woodhouse [84], and Tenny [113]. The results listed in Table 9 are typical of present-day capability in terms of expected accuracy.

The percentage of the analysis falling within specified limits for each investigator are listed in Table 10. The method of evaluation was to calculate, in the manner described later in the section on quantitative analysis, a theoretical intensity ratio, $k(\text{cal})$, from the known alloy composition. The relative error, $\frac{\Delta k}{k}$, is obtained from

$$\frac{\Delta k}{k} = \frac{k(\text{exp}) - k(\text{cal})}{k(\text{cal})} \times 100$$

where $k(\text{exp})$ is the experimentally determined intensity ratio. For investigators reporting compositions, the relative error was $[C(\text{cal}) - C(\text{chem})] \times 100/C(\text{chem})$, where $C(\text{cal})$ is obtained from $k(\text{exp})$. The histogram in Fig. 23 summarizes the data. In Beaman and Solosky's data $k(\text{cal})$ was obtained using the Duncumb and Reed [115] atomic number correction, the Heinrich [116] σ value in the Duncumb and Shields [117] absorption correction, the Reed [118] characteristic fluorescence correction, and the Henoc [119] continuous fluorescence correction. A complete discussion of quantitative correction procedures is presented later. All of the analyzed alloys were carefully polished and have been well characterized with respect to homogeneity and chemical composition.

There are many interesting aspects to

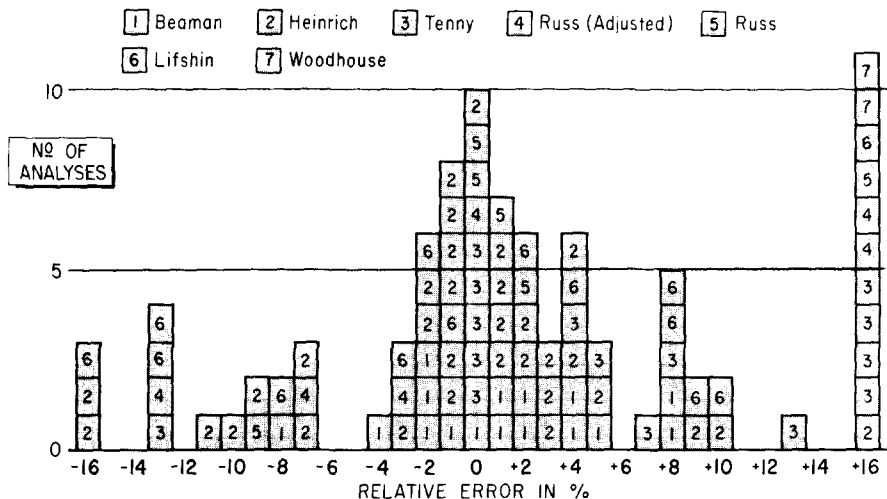


Fig. 23—A histogram displaying the relative errors encountered in 85 quantitative analyses performed with an energy dispersive spectrometer. The legend lists the authors who performed the work, referenced in Table 9. The relative errors are either $100 \times \Delta k/k$ or $100 \times \Delta C/C$, where $\Delta k/k = (k(\text{exp}) - k(\text{cal})) / k(\text{cal})$ and $\Delta C/C = (C(\text{exp}) - C(\text{true})) / C(\text{true})$. The values at the extremities of the histogram are greater than +16% or less than -16%.

these data which should help to establish expected accuracy values at the present time.

1. About 45 percent of the EDS analyses (44 analyses by Heinrich, Myklebust and Heinrich, and Beaman and Solosky using integrated peaks) fell within a range of values of $\Delta k/k$ or $\Delta C/C = \pm 2$ percent, while all of the WDS analyses performed by Beaman and Solosky fell within this range when the alloy composition exceeded 19.9 percent.

2. When the analysis is restricted to compositions above 19.9 percent, integrated peak intensities are used, and the data of Beaman and Solosky, Heinrich and Myklebust, Lifshin, and Tenny (59 analyses) are considered, 37 percent of the analyses were within ± 2 percent and 53 percent were within ± 4 percent. Histograms published by Heinrich [116] and Duncumb et al [120] reveal about 60 percent of the EPA-WDS analyses falling within ± 2 percent and over 80 percent within ± 4 percent.

It should be mentioned that the alloys used in the WDS work were not characterized as well as those used in the EDS work. The rms error for the 59 systems with $C > 19.9$ percent is 7.4 percent, the arithmetic mean is 5.2 percent, and the standard deviation is ± 5.1 percent. The Duncumb et al [120] data had an rms error of about 6 percent. Thus, the accuracy attainable with an EDS is not yet as good as with a WDS, but relative errors of better than ± 6 percent should generally be expected at moderate concentration levels (above 20 percent) in simple alloy systems. This compares with the ± 1 percent recently claimed for the EPA by Poole and Martin [51].

3. The mean of the distribution of 59 alloys with $C > 19.9$ percent is +0.2 per-

cent with 32 positive and 27 negative errors. While there is no significant bias in the distribution, there is definite bias within the individual sets of data, for example, the Myklebust and Heinrich [112] data show a definite positive bias with 13 of 16 errors being positive, and 11 of 15 analyses by Tenny [113] show positive errors.

4. It is generally observed that the relative errors decrease with increasing concentration.

5. The data are insufficient to determine if the use of integrated intensities is superior to using spectral peak intensities less estimated spectral background ($P - B$). Beaman and Solosky have obtained good results using $P - B$ in simple alloys when using long counting periods (600 s).

6. There is a dramatic deterioration of the results obtained at low concentrations. The rms error of 16 analyses with $C < 19$ percent is 138 percent and the mean is +71 percent. There is a definite large positive bias evident which increases with decreasing concentration. Even in the early work of Tenny [113], his lowest measured concentration was in great error. This apparent enhancement makes quantitative analysis at low concentration questionable at best and certainly casts some doubt on the absolute values of the detectable limits mentioned later; thus, one cannot expect to accurately analyze at or near the detectability limit without using standards. The reasons for the enhancement are presently unknown but may be at least partially due to such factors as inaccurate background determinations in

the dilute alloy, deadtime problems that could be dependent upon intensity, and electronic difficulties. Woodhouse [121] has suggested that in some MCAs the lower energy noise pulses will affect the pulse accumulation at higher energies.

The data published by Russ [122] require special attention as they indicate EDS performance superior to any mentioned above. Russ reports that in analyzing 32 brass alloys, all containing Cu, Zn, Fe, Sn, Al, and Pb, 72 percent of the Cu and Zn concentrations (64 total analyses) were within ± 1.5 percent of the true chemical composition. For low level Fe, Sn, Pb, and Al analyses (32 analyses for each element) 69, 62, 62, and 59 percent, respectively, were within ± 1.5 percent. These figures are as good as those encountered in an EPA-WDS system. Russ used the following empirical expression suggested by Ziebold and Ogilvie [123]:

$$C_A/k_A = \alpha_A + C_A (1 - \alpha_A) \quad (5)$$

or

$$\frac{1 - k_A}{k_A} = \alpha_A \frac{1 - C_A}{C_A}$$

where

$$\alpha_K = \sum_{i=A}^n \alpha_{Ki} \frac{C_i}{1 - C_K} \quad (6)$$

K represents the analyzed element and there is an expression of the form of Eq 5 for each analyzed element with a corresponding α_K . When examining Cu in the Cu-Zn-Fe-Sn-Al-Pb alloy,

$$C_{Cu}/k_{Cu} = \alpha_{Cu} + C_{Cu}(1 - \alpha_{Cu})$$

where

$$\alpha_{Cu} = \frac{\alpha_{CuCu}C_{Cu} + \alpha_{CuZn}C_{Zn} + \alpha_{CuFe}C_{Fe} + \alpha_{CuSn}C_{Sn} + \alpha_{CuAl}C_{Al} + \alpha_{CuPb}C_{Pb}}{1 - C_{Cu}}$$

and $\alpha_{KK} = 0$. The α_{Ki} values were determined experimentally by Russ using sintered powders and a large analytical area, a procedure proposed by Moll [124] which is open to question whenever there is negligible or limited solubility.

In Table 11 the best reported results of Russ are shown and the agreement between the EDS determinations and chemical compositions is excellent. We have used Russ's EDS compositions and α_{Ki} values to calculate α_K values (Eq 6), which in turn were used in Eq 5 to calculate $k_{Cu}, \dots, k_{Pb}$. These k values (row 5 in Table 11) then must represent those experimentally measured by Russ. The experimental k values were not part of any of the papers where these data were presented [86, 122, 125]. They were converted to concentrations using the Duncumb and

Reed [115] atomic number correction, Heinrich's [116] σ value in Duncumb and Shields [117] absorption correction, and Reed's [118] characteristic fluorescence correction. The computations were carried out using computer programs written by Beaman [126] and Duncumb and Jones [127]. The results are given in the sixth row of Table 11 and the relative errors are listed in the last row. These errors are more in line with those of other investigators and two of the lower compositions (Al and Pb) do show large positive errors.

The accuracy at moderate concentration levels will improve with a better understanding of the background correction. This understanding is essential if background spectra are to be extracted by a computer from experimental measurements. In our own work it has been possible to occasionally improve the accuracy by measuring the variation of background intensity, in an energy interval corresponding to the line of interest, with atomic number and then calculating the background contribution. The excellent work of Rao-Sahib and Wittry [128, 129] in measuring the X-ray continuum will help in the solution of these problems. The apparent enhanced emission at low concentrations is a serious problem that presently poses severe limitations on accuracy.

The accuracy attainable in an SEM-EDS combination may be affected by the fact that SEMs are designed in such a manner that non-normal electron beam incidence is used to promote contrast. Non-normal incidence and its effect on quantitative results has been a subject of debate for several years in the field of EPA. In quantitative analysis non-normal electron incidence has often been corrected for by using an effective take-off angle ϵ . This angle is given by $\epsilon = \csc^{-1}[(\sin \theta)(\csc \psi)]$ where θ is the acute angle between the incident beam and the specimen surface. Duncumb and Jones [127] state that the accuracy of such a procedure is unknown. Green [130] and Brown [131] have questioned such a simple relationship between $f(\chi)$ and θ . Bishop [132] has found that the factor $(1 - 0.5 \cos^2 \theta)$ accounts for the observed variation of $f(\chi)$ curves with the incident angle θ . ($f(\chi)$ is the fraction of generated intensity that is emitted at the surface of a target and will be discussed in the section on quantitative analysis.) In this case ϵ is given by $\epsilon = \csc^{-1}\{(1 - 0.5 \cos^2 \theta) \csc \psi\}$.

Bishop [133] was not able to use this simple relationship to account for the $f(\chi)$ variation with θ obtained from Monte Carlo calculations. Abelman and Jones [134] found both expressions for ϵ inadequate. Colby, Wonsidler, and Conley [135] reported that experimental probe ratios, measured in two instruments (one with normal and one with non-normal inci-

Table 11—Computations Based on Data of Russ* (Brass Samples at 40 kV, $\psi = 43$ deg.)

Element	Compositions, k values and relative error in %						
	Cu	Zn	Fe	Sn	Al	Pb	Total
Chemical composition	65.4	21.3	2.3	3.4	4.2	3.7	100.3
Composition-EDS	65.1	21.5	2.3	3.1	4.3	4.3	100.6
$\Delta C/C^1$	-0.5	0.9	0	-8.8	2.4	16.2	-
k calculated ²	58.4	18.1	2.6	2.5	1.0	4.2	86.8
C from k ³	60.5	18.5	2.3	3.3	6.6	7.5	98.7
$\Delta C/C^4$	-7.5	-13	0	-2.9	+57	+103	-

*References 86, 122, and 125.

1) $\{C(EDS) - C(true)\}/C(true)$; 2) using α_{ki} values from Russ (86);

3) composition calculated from k calculated; 4) $\{C(calc) - C(true)\}/C(true)$;

dence), were correctable, using a specific correction scheme, to the same value within experimental error and that no bias was observed. They used $\epsilon = \csc^{-1}[(\sin \theta)(\csc \psi)]$ and made measurements in three alloy systems. Duncumb [25] expects negligible effects in quantitative corrections, using an effective take-off angle, as long as θ is more than 45 deg. Experimental $f(\chi)$ and backscatter data will help to establish the range of validity of the simple expressions for ϵ .

Not all SEMs allow normal electron beam incidence in the EDS mode, and even when the specimen geometry is known the X-ray take-off angle is not always readily apparent. In order to obtain good results with our Cambridge Stereoscan it was necessary to derive an analytical expression relating the tilt angle t , specimen height, specimen translation, and the specimen to crystal distance to the X-ray take-off angle, ψ . In the simplest case we found $\sin \psi = 0.707 \sin t$. In contemplating the use of an SEM as an EPA, knowledge of the take-off angle is essential and the most desirable situation would include the capability of returning with good precision (0.1 deg) to zero tilt. This should be easy to attain at zero tilt (normal electron beam incidence), but it would be more difficult to know any other tilt angle to this degree of accuracy.

Precision—The expected precision in a measured X-ray intensity ratio based purely on random counting statistics (Poisson) is given by

$$\frac{\sigma_k}{k} \geq \pm \left(\frac{P' + B'}{(P' - B')^2} + \frac{P^0 + B^0}{(P^0 - B^0)^2} \right)^{1/2} \quad (7)$$

The greater than symbol indicates that in practice the experimental precision is not as good as the counting precision due to other random errors in the systems (current and voltage fluctuations, specimen and beam positional stability, etc.). The question that arises in predicting EDS precision is whether or not the high sensitivity (P)

offsets the relatively high B (low P/B ratio). In Fig. 24 the theoretical precision, σ_k/k from Eq 7, is plotted as a function of the counts accumulated on the standard (P^0) for five concentration values ($P'/P^0 = 1, 5, 10, 50$, and 90 percent) and two P/B ratios (50 or 1000) at each concentration. In the calculation, the backgrounds on the alloy (B') and standard (B^0) are assumed to be equal, a valid assumption in this approximate calculation. In actual analysis the precision can be improved by the proper distribution of the total counting time between P^0 , P' , B^0 , and B' [136].

From Fig. 24 it is clear that for equal count times the P/B ratio does significantly affect the precision, particularly at low concentrations. It is also clear why the precisions reported for EPAs ($P/B = 1000$) are in the range of 0.5 to 1 percent. In quantitative work on Cu-Zn, Cu-Au, and Ti-Nb with a WDS, calculated precisions of 0.1 to 0.3 percent corresponded to observed precisions of 0.3 to 0.6 percent. The high P/B ratio, combined with a stability that easily allows the use of counting intervals up to 500 s, provides good precision even at low concentrations. The low P/B of the EDS can be easily overcome by accumulating more counts, which will actually require less time than the WDS.

Problems arise in trying to compare EDS and WDS by having the WDS operate at a current level where it is not designed to operate. For example, for an accumulation time of 60 s at 1 nA typical σ_k/k values for EDS and WDS would be 2 and 5 percent, respectively; however, running the WDS at 10 nA would reduce the 5 percent to 1.5 percent. This exercise shows that the low P/B in the EDS will not limit its precision. The EPA-WDS combination provides the needed precision at all concentration levels. The EDS can provide equal or better precision at moderate to high concentrations; the question of precision at low concentrations is irrelevant in view of the present accuracy limitations. In summary both devices can provide the

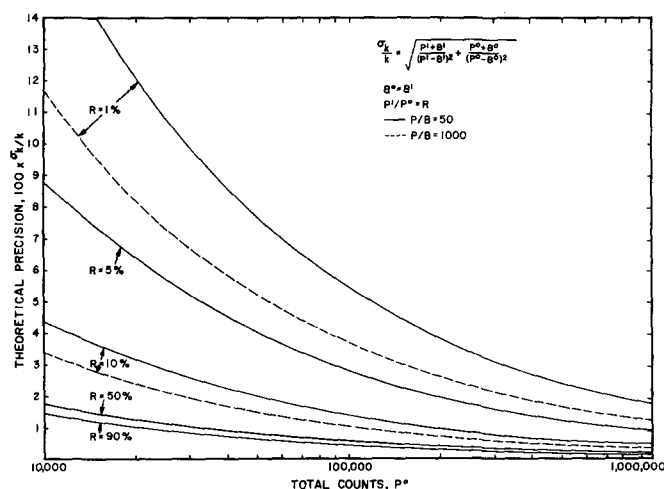


Fig. 24—The theoretical precision, σ_k/k , in the measurement of an X-ray intensity ratio, k , as a function of the total counts accumulated on the standard, P^0 . Curves are shown for two different peak to background, P/B , ratios at five R values, where $R = P'/P^0$. A P/B value of 50 is assumed to be typical of an EDS system, while 1000 is assumed to represent a WDS system. The expression for σ_k/k established by Poisson statistics is shown on the graph.

precision required in quantitative analysis, but the EDS does not yet provide satisfactory accuracy at low concentrations.

At this point let us briefly summarize the present status of quantitative analysis with an EDS.

1. It is possible to quantitatively analyze flat, polished specimens with an expected accuracy of ± 6 percent of the amount present when the concentration exceeds 20 percent, there are no serious interferences, and $Z \geq 12$.

2. At lower concentration, large errors have often been encountered and, therefore, must be expected.

3. The effective take-off angle must be used in converting k values to composition when analyzing flat, polished surfaces with non-normal electron beam incidence. The take-off angle may not be well defined in an EDS because of the large active crystal area.

4. Quantitative reliability will only improve if a better understanding of the background correction is attained. The contribution to background from different sources (detector, continuum, interfering lines) should be carefully measured in different materials. The dependence of background intensity on tilt angle in a SEM should be studied.

5. Integration over a fraction of the peak (about 1.2 FWHM) and simple net intensities ($P - B$) presently provide similar results.

6. There is a need for a versatile computer program to provide unambiguous peak identification and amplitude through deconvolution of the energy spectrum.

7. Accurate analysis in the vicinity of the detectability limit without the use of standards of a similar composition is not presently possible.

8. On rough surfaces a great deal of care and understanding will be required and the accuracy will be hampered by non-normal beam incidence and a lack of knowledge of the take-off angle.

9. Satisfactory precision is easily attainable, but care must be taken to insure that a sufficient number of counts are accumulated in each peak of interest. Experimental work is needed to determine how close the experimental precision is to the theoretical precision in an SEM-EDS when using currents below 1 nA.

Detectability Limits—The most commonly discussed aspect of EDS is the limit of detection, $C(DL)$, which has been shown by Ziebold [137] to be

$$C(DL) = \frac{3.29\alpha}{[nTP(P/B)]^{1/2}} \quad (8)$$

where α is the empirical constant in the Ziebold and Ogilvie [123] expression (Eq 6); nT is the total time of the measurement, that is, the product of number of determinations and the time per determination; P is the peak intensity from a pure solute; and P/B is the peak to background intensity ratio, taken to be that for the pure solute (the best possible condition). Because α is only a function of the material and operating conditions, to compare the detectability limits for WDS and EDS it is only necessary to consider $P \times P/B$, the best $C(DL)$ being provided by the maximum P^2/B . It is important to note that the accuracy or precision of the determination of concentrations at or near the detectability limit is ignored in this discussion. The obvious conflict is between the high P/B and low P of the WDS and the high P and low P/B of the EDS. The

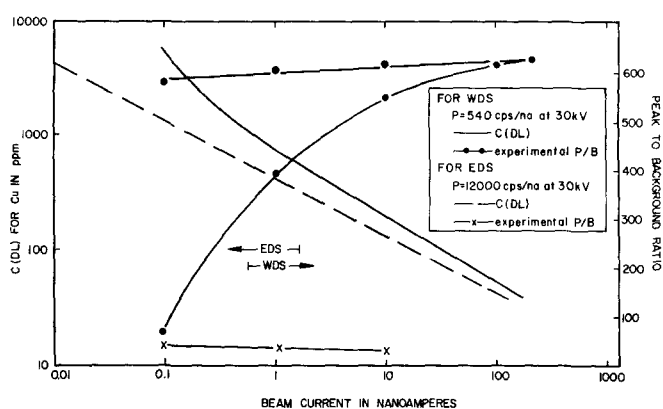


Fig. 25—Calculated values of the detectability limit, $C(DL)$, for Cu as a function of electron beam current. The upper $C(DL)$ curve represents conditions encountered with a WDS, namely, a sensitivity of 540 cps/nA and the P/B values shown on the right-hand axis. The lower curve represents conditions encountered with an EDS, namely, a sensitivity of 12000 cps/nA and a P/B value of about 50. Experimentally measured P/B values for Cu are plotted on the right-hand axis as a function of beam current. For the WDS the upper P/B curve includes a correction for electronic noise, while the lower does not. Detectability values were calculated from Eq 8.

favorite procedure is to compare P^2/B values using the type of performance data presented earlier in Table 7; experimental data are much more scarce. Care must be exercised in using P^2/B data because in practice one does not measure $C(DL)$ using pure materials but rather localized regions in complex matrices.

In Table 12, P^2/B values calculated using the experimental data of Table 7 and a beam current of 1 nA are presented. The variation between the different investigators, partially due to the use of different operating conditions, solid angles, collimation, etc., makes it hazardous to venture a statement concerning the detectability of WDS versus that of EDS. At a low atomic number the WDS is about as good as the EDS, whereas at a higher atomic number the EDS gives higher P^2/B values at a beam current of 1 nA. While there is no limit to the number of such calculations one can make, there are instrumental limitations that make continued calculations futile, and in one's eagerness to prove one device superior it is possible to leave the realm of present-day reality. Existing EDSs fail to function properly when the counting rates reach a certain level, usually around 10,000 to 30,000 cps due to pulse pile-up and dead-time problems (reached at about 1 nA). WDSs, on the other hand, work well up to 100,000 cps.

In Fig. 25 the calculated detectability limit for Cu based on Eq 8 is plotted as a function of beam current for the EDS and WDS. Because the peak intensity is proportional to the beam current, $C(DL)$ decreases with increasing current. The EDS data are calculated using a sensitivity of 12,000 cps/nA and a constant experimental P/B ratio of 50; the WDS

Table 12—Calculated Values of P^2/B Based on Experimental Data from Energy and Wavelength Dispersive Spectrometers

Author Reference Spectrometer		Russ 86 EDS	Sandborg 87 EDS	Sutfin 138 EDS	Russ 48 EDS	Sutfin 138 WDS	Russ 86 WDS	Beaman WDS	Kimoto 88 WDS
P ¹	Element	7600	4270		1300		700	400	2400
P/B	Al	160	81		7		1200	3000	1500
$10^4 P^2/B$		120	32	16	1	64	84	120	360
P	Ti	16600	12000		10000		1100	500	1800
P/B		135	77		22		1500	2000	700
$10^4 P^2/B$		220	92		22		165	100	125
P	Cu	11600	10400 ²		14000		250	540	1000
P/B		104	77		16		400	550	300
$10^4 P^2/B$		120	80		22		10	30	30
P	Mo	1220	2600				30	40	
P/B		47	21				40	100	
$10^4 P^2/B$		6	5				.1	.4	

1) P is integrated cps/nanoampere in EDS systems and cps/nanoampere in WDS systems; 2) Fe.

data are calculated using a sensitivity of 540 cps/nA and the experimental P/B ratios shown in Fig. 25. The low P/B values in WDS at low currents are due to a significant electronic noise contribution. After correcting for this effect, the P/B values are given by the uppermost P/B curve. At 12,000 cps/nA, the EDS would not be useful much above 1 nA because of electronic failure at high counting rates, while the WDS would not be useful much below that current. In the range where the two overlap (0.5 to 5 nA), the EDS would provide $C(DL)$ values 100 to 600 ppm lower than the WDS for Cu. However, the minimum absolute detection limit could not be realized with the EDS, that is, it would fail to work well in the vicinity of 300 ppm, while the WDS could measure Cu in the appropriate matrix at the 50-ppm level. In the case of Al, $C(DL)$ -WDS/ $C(DL)$ -EDS = 0.44 when Sutfin's [138] EDS and Beaman's WDS data at 1 nA are used. Thus, at low currents the absolute detection limit is higher and the EDS is superior, while at high currents the absolute detection limit is lower and the WDS is superior. Once again the two devices appear to be complimentary rather than competitive.

It is important to note that on an SEM with a high sensitivity EDS (large solid angle) it will not be possible to attain the low detectability limits commonly reported for the EPA-WDS combination. Thus, the simple comparison of P^2/B values can be misleading. Spectral interferences with the EDS are most troublesome when analyzing low concentrations, and in many practical cases detection limits will be far above those calculated from Eq 8 because of the relatively poor spectral resolution. Up to this point, spatial

resolution has been neglected and in many cases what will be sought is the $C(DL)$ at a particular level of resolution. Yet, as has been shown, the resolution degrades rapidly with increasing current. Cases will arise where the low current high resolution capability of the EDS will be indispensable.

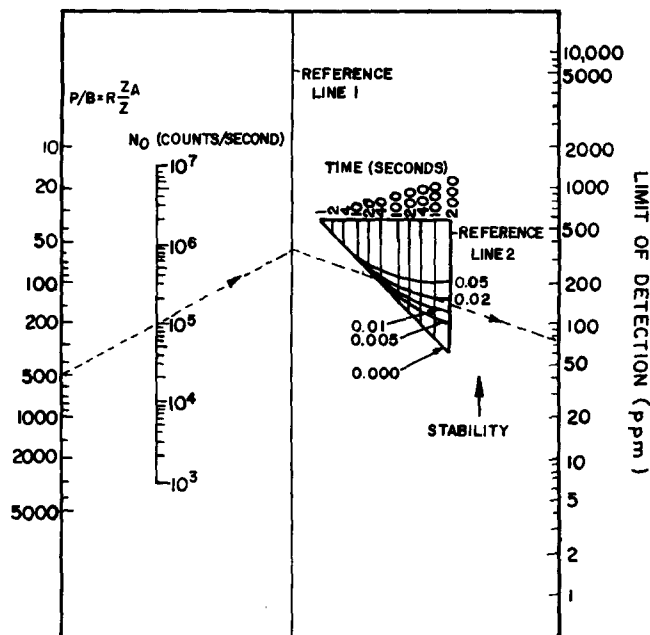
Returning to reality, let us consider the actual attempts that have been made with EDS to measure $C(DL)$ in alloy systems. Calculations of P^2/B values are abundant whereas experimental determinations of $C(DL)$ are scarce. Eichen et al [139], using an EDS with a 325-eV detector in a JEOL SEM ($\psi = 35$ deg) and a series of well characterized alloys of diminishing concentration, reported the following $C(DL)$ values: 0.25 percent Au in Al-Au, 0.5 percent Cu in Al-Cu, and, 3.0 percent Ni in Fe-Ni; all at 35 kV, 1 nA, and 300 s accumulation time. At 25 kV, 1 nA, and 300 s accumulation time, the limits in the same alloys increased to 1 percent Cu, over 2 percent Au, and 3 percent Ni. Increased counting times and higher currents did not appreciably affect these results (the compositional steps in the alloys were 0.25 to 1 percent). The Fe $K\beta$ interference is responsible for the high $C(DL)$ for Ni, which values could be lowered by using a higher resolution detector.

Lifshin [140] has measured $C(DL)$ for Si, Mn, Ni, Cr, Mo, V, and Cu in six steel standards using an EDS in an EPA at 20 kV with 5 nA beam current and 600 s accumulation time. While the minimum detected concentrations varied with steel composition, the results can be summarized as follows. Concentrations detected without spectrum stripping were (in percent) about 0.1 Si, >1.4 Mn, >5.1 Ni, 0.3 Cr, 0.2 Mo, 0.3 V, and 0.5 Cu. With spectrum stripping the Mn, Ni, and Cr

$C(DL)$ values were lowered to 1.1, 0.6, and 0.2 percent, respectively. These experimental values are considerably higher than those indicated in the calculations above and serve to illustrate the problems of spectral interference.

The $C(DL)$ values predicted in 1969 by Ogilvie [141] of 2000 to 5000 ppm are in line with what is being found experimentally. In an EPA-WDS system, the experimental $C(DL)$ values would, for these elements in steel, be in the range of 50 to 1000 ppm (notwithstanding a low solid angle) and there is an abundant literature verifying such detectable limits [51]. Bayard [142] reports typical $C(DL)$ values of 5000 ppm using an EDS compared to 50 ppm using a WDS. The accuracy and precision of the $C(DL)$ work done with the EPA has been good when standards are used. Biloui et al [143] have reported detectability limits of about 10 ppm Fe, Cu, and Si, in Al, and reports in the range of 50 to 250 ppm are not uncommon. Kniesly et al [144] have detected rare earth impurities at the ppb level using cathodoluminescence [144]. We believe that, presently, statements implying low $C(DL)$ values for EDS [145] are not applicable to a broad range of commercial materials.

The data of Eichen et al [139] illustrate the significant dependence of $C(DL)$ on the acceleration potential, which arises because of the increase in P/B ratio with acceleration potential in bulk materials. Green and Cosslett [146] have shown that P/B is proportional $(E_0 - E_c)^{0.63}$ for a given bulk material. Elad et al [108] have experimentally measured P/B as a function of acceleration potential for Cu with an EDS and found the P/B ratio to vary from about 3 at 10 kV to 42 at 45 kV. Un-



fortunately the spatial resolution degrades seriously with increasing acceleration potential.

Long [147] has published an interesting nomogram for determining the minimum detectable concentration from the P/B ratio for the specimen, the count rate for a pure standard, the total counting time, and the beam current stability (typically <1 percent). He describes the use of his nomogram, shown in Fig. 26, as follows:

The nomogram is used by placing a rule through the P/B figure for the specimen (RZ_A/Z) and N_0 so as to intersect the reference line 1. A point on reference line 2 is then found by projecting horizontally the point of intersection of the counting time and the appropriate stability curve. A straight edge placed on the two points obtained on the reference lines will then enable the limit of detection to be read off from the extreme right-hand scale.

Such calculations, however, ignore matrix effects.

Energy Resolution versus Sensitivity and Crystal Area—The sensitivity (cps/nA) and therefore $C(DL)$ of an EDS can be improved by increasing the solid angle. This is most easily accomplished by increasing the active detector area [148, 149]. Unfortunately both the resolution and P/B ratio degrade with increasing area so that in the selection of the size of detector a trade-off between resolution and sensitivity must be made. Qualitatively, since the P and B intensities are proportional to the area, the sensitivity increases with area and the detectability limit decreases as $1/\sqrt{\text{area}}$; however, this simple picture must be modified by the fact that the P/B ratio decreases with area.

Frankel and Aitken [148] have pursued these problems in detail and their work shows that the gain in sensitivity P more than offsets the reduction in P/B (see Fig. 27) caused by the degraded resolution, and the higher the energy the more this is true. Thus $C(DL)$ does decrease with increasing area. They [148] also effectively show that the loss of resolution is almost totally an area effect rather than a result of increased intensity, for example, the resolution loss in going from 10 mm² to 80 mm² at 1000 or 8000 cps is about 15 eV. The question that must be answered is whether or not the loss of resolution indicated in Fig. 27 can be tolerated. Undoubtedly there are many cases where high resolution is not essential and the increased sensitivity and reduced detectability accompanying an area increase would be most welcome; however, most analysts encounter problems that have varying resolution requirements and frequently the resolution will be the limiting factor in the analysis. For this reason, throughout the discussions we have taken the viewpoint that the analyst would usually require the crystal with the maximum resolution. It is possible that with a better understanding of the background intensity and the development of a reliable computer program for analyzing the energy spectrum that some resolution could be sacrificed for important gains in sensitivity. Most existing SEMs are being equipped with 6-mm-diameter crystals as a compromise between the low current capability and resolution. The choice is more difficult in the EPA, where those analysts needing small crystals because their instrument does not function well at low currents use 4-mm crystals while those

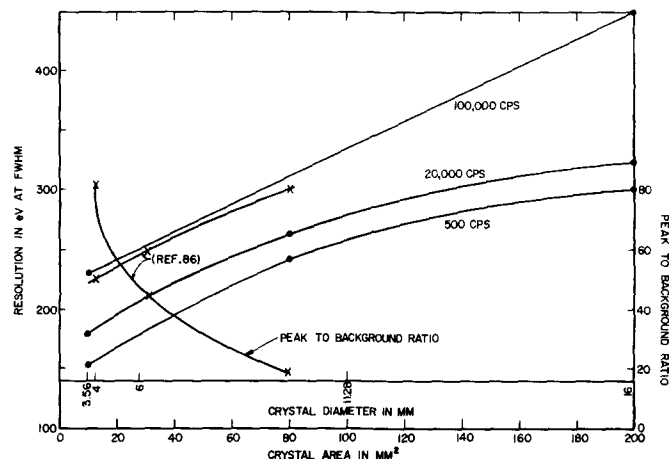


Fig. 26—A useful nomogram for calculating the statistical limit of detection (from Long [147]). In the figure, a P/B ratio of 500, a count rate of 10000 cps on the pure solute, a beam current stability of 1 percent, and a total counting time of 400 s lead to a predicted detectability of 75 ppm. (left)

Fig. 27—The effect of the area of a Li drifted Si detector on EDS resolution and on the P/B ratio. Using the left-hand axis, the resolution at FWHM is plotted as a function of active crystal area for total spectrum counting rates of 500, 20,000, and 100,000 cps (data from Frankel and Aitken [148]). Using the right-hand axis, the P/B ratio is plotted as a function of active crystal area (data from Russ [86]).

seeking maximum sensitivity to complement the WDS use 6-mm crystals.

This brings up the question of how much resolution is needed. Frankel and Aitken [148] have established some useful guidelines assuming a gaussian distribution and ignoring the tails. If ΔE is the energy between the peaks to be separated, the FWHM resolution must be less than the indicated percentage of ΔE to provide the indicated peak/valley intensity ratio, where the peak intensity is that of the lowest peak. The FWHM must be 61.5 percent of ΔE for a peak/valley ratio of 4/3, 57 for one of 2/1, 53.5 for 4/1, 28.6 for full separation, and 67 for 2/1 with peaks of equal height. Thus, if the problem were the Cu $K\beta$ -Zn $K\alpha$ interference ($\Delta E = 274$ eV), the FWHM resolution would have to be 78 eV for full separation and 168 eV for a peak/valley ratio of 4/3.

Spatial Resolution—The most intriguing prospect of an EDS-SEM combination is that of possible chemical analysis of extremely small areas. In a SEM the beam diameter can be reduced to the order of 100 Å, compared to the 1000 to 3000-Å limit in an EPA; however, it is not often that an EPA can be operated at its minimum possible beam size and still provide sufficient X-ray intensity. Thus, rather than using a 2000-Å beam, one 0.5 μm in diameter is commonly used to achieve sufficient current and satisfactory X-ray statistics. The improved sensitivity of an EDS (10 to 50 times as great as that of a WDS in an SEM) permits the use of currents 10 to 50 times as small as those used in an EPA for the same emitted X-ray intensity (disregarding P/B). The factor of 10 to 50 is considerably less than the factor of 1000

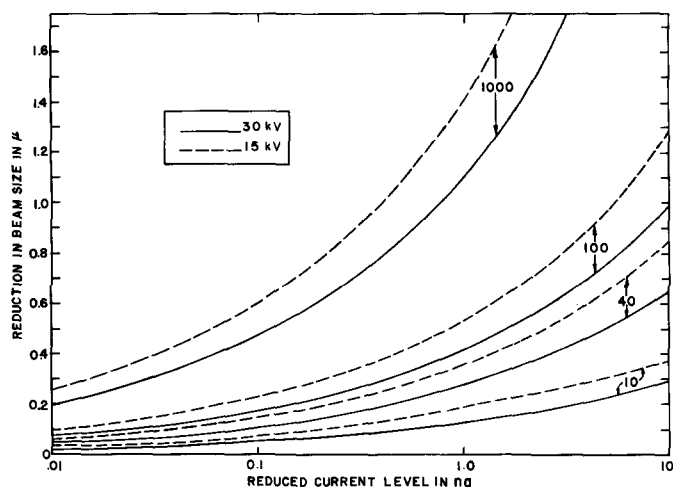


Fig. 28—The reduction in the electron beam diameter accompanying a reduction in beam current. This reduction in diameter is plotted as a function of the reduced current level for reduction factors of 1000, 100, 40, and 10 at two different values of E_0 . For example, if the beam current at 15 kV is reduced by a factor of 100 to 0.1 nA, the incident beam size will be 0.225 μm less than it was at 10 nA. The solid curves are for 30 kV and the dashed curves are for 15 kV.

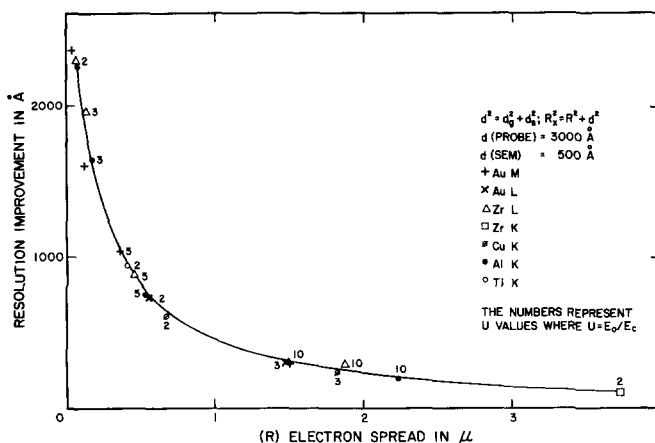


Fig. 29—Possible improvements in resolution as a result of reductions in the incident beam diameter. The improvement in resolution accompanying a decrease in beam diameter from 3000 to 500 $\text{\AA}$ is plotted as a function of the electron spread, R , for five different elements. The numbers adjacent to the points indicate the overvoltage, U , where $U = E_0/E_c$. In the analysis of Cu using the Cu K α line and an overvoltage of 2 ($E_c \approx 9$, $E_0 = 18$), the electron spread would be 0.68 μm and an improvement in resolution of 600 $\text{\AA}$ would occur if the incident electron beam diameter were reduced from 0.3 μm to 500 $\text{\AA}$.

sometimes suggested and is based on the experimental data of Table 7, where the ratio of the EDS and WDS sensitivities (cps/nA, using Russ's data) are 11, 15, 46, and 40 for Al, Ti, Cu, and Mo, respectively. Unfortunately, in most cases the X-ray resolution is predominantly determined by electron scattering, which is independent of incident electron beam size and current and depends only on E_0 and Z .

Figure 28 is a plot of the reduction in incident electron beam size that will result from lowering the beam current by various factors (10, 40, 100, 1000) to the indicated reduced current level. The indications are that, to maintain satisfactory sensitivity levels, EDS-SEM operation will have to be in the 0.1-nA range, corresponding to a reduction in incident electron beam size of 2000 $\text{\AA}$ or more. An example will serve to illustrate what this means in terms of ultimate X-ray resolution. If Cu is being analyzed and 2500 cps are required for satisfactory statistics, 10 nA would be required with a WDS and 0.25 nA with an EDS. At 30 kV the incident beam size, d , would be reduced from 0.21 μm at 10 nA to 0.05 μm at 0.25 nA. At 30 kV the total spread due to electron scattering, R , in Cu would be about 2 μm (see Fig. 10). There would then be a negligible improvement in resolution because $R \gg d$. At 15 kV the reduction in d would be from 0.28 μm at 10 nA to 0.07 μm at 0.25 nA and, since the spread is about 0.5 μm , a gain in resolution of about 1000 $\text{\AA}$ could be realized at the lower current level. In some problems such a gain could mean the difference between success and failure.

Resolution gains can only be realized when d represents a significant portion of

R , that is, when R is small, which occurs when the overvoltage ($U = E_0/E_c$) and, therefore, acceleration potential are low. In Fig. 29 the gain in X-ray resolution accompanying an electron beam diameter reduction from 3000 $\text{\AA}$ to 500 $\text{\AA}$ (corresponding to a current reduction from 12 nA to 0.1 nA at 30 kV) is shown for six X-ray lines and four overvoltages as a function of the lateral spread (Eq 4). Gains of 2000 to 3000 $\text{\AA}$ over those obtainable with a WDS will be possible only at $U < 2$ and with longer wavelength radiation. The use of increasing acceleration potentials to increase P/B ratios or improve sensitivity would rapidly negate any resolution gains. Generally speaking, operation at normal overvoltages of 2 to 3 will provide resolution gains ranging from 0 to 2000 $\text{\AA}$ (highest gain at longest wavelength) and permit the analysis of particles down to about 0.3 μm . Improved X-ray images will also be possible. Only slightly better resolution could be attained by further current or voltage reductions, which would result in serious intensity losses and subsequent degradation in precision.

Mass Sensitivity—With respect to the question of mass sensitivity (the amount, grams, of material present at the detectable limit of the technique), it is not possible to generalize because of the strong dependence of electron scattering on atomic number and acceleration potential. When R is large compared to d , the WDS will provide the lowest mass sensitivities, because the experimental $C(DL)$ values seen for EDS are discouragingly high compared to those indicated theoretically. EPA-WDS mass sensitivities range from 10^{-15} to 10^{-18} g. When resolution gains

can be achieved through low voltage operation with R and d both small and of similar magnitude, the reduction in excited volume could result in mass sensitivities ranging from 10^{-16} to 10^{-17} g.

To offer a generalization, we believe that in most practical problems the WDS will provide lower detectability limits and higher mass sensitivities. It is worth noting that the mass sensitivity of the ion mass analyzer is on the order of 10^{-19} g. Table 13, listing the disadvantages of the EDS, serves as a summary of the discussion just completed. There is no doubt that improvements in the detectors and electronics of energy dispersive spectrometers will occur and that the EDS will play an increasingly important role in quantitative microanalysis.

Combination Instruments

EPA with SEM Capabilities versus SEM with EPA Capabilities—The decision as to which instrumental combination is the most useful is not the same in every case. In making recommendations we assume that there is a need for accurate chemical analyses for all elements B through U. If there is a large amount of imaging and accurate analytical work to be done, it would be advisable to have both an EPA and an SEM. Because analytical work (EPA) usually consumes a great deal more time per problem than does imaging (SEM), a severe reduction in the amount of SEM imaging carried out will occur if a large analytical work load is encountered. If sufficient funds are available, an SEM-EDS in addition to an EPA-

Table 13—The Disadvantages of an Energy Dispersive Spectrometer

Low sensitivity in EPA

.0001 steradian solid angle.

Operation at cryogenic temperatures required

large cryostat.
must maintain liquid nitrogen supply.
microphonics can degrade resolution.

Isolation required - Be window

absorption of long wave lengths.
limits analysis to $z > 10$.

Poor spectrometer resolution

serious interferences at low energy.
computer reduction of spectrum required.

Non-discriminating to x-ray sources

backscattered electron excitation of remote areas.
excitation of extraneous signals in instrument components.
secondary excitation of remote sample regions.

Quantitative capabilities

fair accuracy in absence of severe interferences at moderate concentration levels ($C > 20\%$).
poor accuracy encountered at low concentrations.
computer reduction of raw data required to allow analysis in presence of energy interferences.
background correction not well understood.
erroneous results possible because of above and absorption in remote areas of the sample.
in some SEMs quantitative work is subject to uncertainty due to non-normal electron beam incidence.
accurate knowledge of x-ray take-off angle not always available.

Intensity sensitivity

can occur at total spectrum count rates as low as 10000 cps.

WDS-EDS with good secondary electron detection (resolutions $< 1000 \text{ \AA}$) would be a useful combination. The problem of choice becomes more acute when it is necessary to purchase a single instrument because of limited funds or workload. We believe that at present the best single instrument would be an SEM-EDS-WDS combination.

The SEM-EDS-WDS combination is preferred over existing EPA-EDS combinations, because in the SEM mode most existing EPAs do not provide satisfactory imaging performance. However, two EPA manufacturers have recently announced resolution capabilities in the secondary mode in the order of about $500 \text{ \AA}$. Conversion of existing EPAs into high quality SEMs is difficult because of improper shielding (stray fields) and excessive vibration (stage design). The resolution in the secondary mode typically runs to values of 1000 to $2000 \text{ \AA}$, as compared to 100 to $250 \text{ \AA}$ in an SEM, and EPA stages do not generally possess the versatility essential for good SEM work, once again because of the limited working distance. In addition, most SEMs are easier to operate and maintain and are often less expensive than EPAs.

Requirements for a Satisfactory SEM-EDS-WDS Combination/ When selecting a single instrument for an SEM-EDS-WDS combination, remember that it must overcome the problems associated with the conversion of an SEM to an EPA. (1) A broad useful current range must be available, say, 10^{-14} to 10^{-6} A . This current must be continuously variable and measurable at any E_0 . Variable aperture selection will be necessary. The C_s should be such as to provide optimum current density over the entire range of currents. (2) It should be possible to analyze the specimen with normal electron beam incidence, this means that the apparatus should return to zero tilt with sufficient precision. The EDS should be positioned to give high sensitivity at zero tilt. (3) It should be possible to view the specimen with an optical microscope during analysis; still, the light optical system would not have to be of as high a quality as those in some EPAs nor would the light and electron axes have to be coincident. (4) The X-ray take-off angle should be accurately known for any tilt angle for both the EDS and WDS. (5) There should be room for anticontamination devices. (6) Several optional features, such as normally found on an EPA, that would be desirable include X-ray imaging, step scanning, specimen current imaging, line scanning, and chart recording. (7) The WDS used in this combination instrument should preferably consist of two

fully focusing spectrometers with a wide choice of crystals covering the entire wavelength range. It must be possible to easily place the target on the Rowland circle. While a semifocusing WDS does minimize defocusing problems, the use of such a device on a combination instrument degrades the performance in the EPA mode of operation.

Table 14, which lists several commercial SEMs, indicates that most manufacturers are now making WDS accessories available. Any commercial SEM can be equipped with a complete EDS system, including an MCA, at a cost in the range of \$13,000 to \$20,000.

Expectations for the Next Generation of Instruments/ As new instruments with total capability become available, it will be irrelevant whether one has an SEM with EPA capabilities or an EPA with SEM capabilities. The price tag on such an instrument will probably be in the \$110,000 to \$130,000 range. One can expect in either instrument improved vac-

uum systems; human engineering aimed at ease and comfort of operation; better crystals; proportional detectors with better resolution and less intensity sensitivity; higher gun brightness; higher resolution EDS, primarily through preamplifier improvement and cryogenic design; better scanning images and TV scanning; EDSs that function without such serious degradation at high counting rates; higher solid angles for the EDS; objective lenses that provide more room in the vicinity of the specimen; self-cleaning apertures; computer control and automatic data acquisition; highly stabilized beam currents; more rugged and reliable construction; more accessory equipment, such as Auger spectrometers (for low Z and surface analysis); *in situ* ion bombardment; high X-ray take-off angles; energy analyzers for transmitted electrons; detector windows that are more transparent and reliable; better electronics for standard counting channels, that is, low deadtime and high reliabil-

ity; improved programmed spectrometers (WDS); automatic column alignment; automatic focusing; interchangeable stages (transmitted light, cathodoluminescence transmission electron microscopy); and a matrix scanner and quantitative metallography capability.

In addition to such super instruments, inexpensive (<\$25,000) EPAs and SEMs with limited capabilities will undoubtedly appear. One manufacturer has recently announced the availability of a mini-microprobe with a base price below that \$25,000 figure, a 10- μm geometric beam, a weight of less than 150 lb, and an EDS for analysis.

TEM Capabilities/ An obvious extension to existing instrumentation is the addition of a transmission electron microscope capability to the instrument. One EPA manufacturer has done a satisfactory job of this without degrading probe performance and provides a maximum magnification of 10,000 with 50- $\text{\AA}$ resolution. One SEM manufacturer offers satisfactory TEM capabilities, providing a maximum magnification of 100,000 with 30- $\text{\AA}$ resolution. Unfortunately, the maximum potential in these instruments is 50 kV, which restricts the use of the TEM capability to replicas, extremely thin films, and some biological specimens.

While such a combination is useful, the idea of being able to analyze the chemistry (probe), microstructure (high resolution electron microscopy), and crystallography (electron diffraction, crystal structure and orientation) of more conventional (thicker) thin films is certainly an appealing one and has served as the motivation for the development by Duncumb [150], starting in

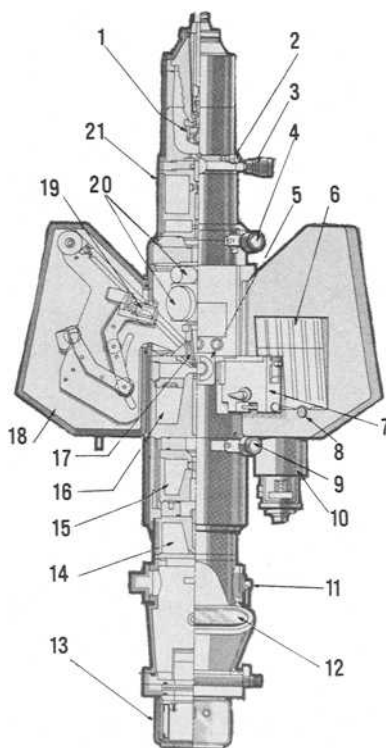


Fig. 30—A schematic diagram of a combination electron microscope-microanalyzer (EMMA). The schematic of the most recent model available, EMMA 4, was provided by Agar [151]. (1) Electron gun; (2) anode plate control; (3) gun aperture; (4) condenser aperture control; (5) specimen selector and tilt control; (6) direct element read-out; (7) specimen airlock; (8) crystal changer; (9) diffraction aperture control; (10) gearbox for servo-control fast-slow scan; (11) high resolution diffraction stage port; (12) viewing chamber; (13) plate camera; (14) projector lens; (15) projector lens; (16) objective lens; (17) minilens; (18) spectrometer 1; (19) crystal holder; (20) beam deflector collis; (21) double condenser lens system.

1962, of a combined electron microscope and electron microprobe known as the EMMA—electron microscope microanalyzer. The outcome of Duncumb's work is the recent appearance on the market of an instrument called EMMA 4, which is shown in Fig. 30 [151, 152]. This instrument can be operated at 40, 60, 80, or 100 kV, provides an optimum resolution of 10 $\text{\AA}$, has a maximum magnification of 160,000, has an electron beam which can be focused to 1000 $\text{\AA}$, and can analyze all elements with $Z > 11$ using two fully focusing linear spectrometers with $\psi = 45$ deg. Thus, the instrument incorporates all the capabilities of a high quality TEM (high resolution microscopy and electron diffraction) and a microprobe (high resolution microanalysis). In 1967 Schippert, Moll, and Ogilvie [153] described a combination TEM-EPA instrument with the following specifications: 0.2- μm beam diameter, 50- $\text{\AA}$ resolution, a magnification of 17,000, variable acceleration from 0 to 75 kV, a WDS with a mica crystal, and an EDS with a proportional detector.

One of the best examples of the vast potential of a TEM-EPA combination is the work done on solute depletion in the vicinity of grain boundaries. In Al-Zn-Mg alloys many attempts have been made to correlate the stress corrosion susceptibility of the alloy to the grain boundary microstructure [154]. The extent of the precipitate-free zone around the grain boundary is generally less than 1 μm and depends upon the alloy composition, quench rate from the solution heat treating temperature, aging time, and aging temperature. It has been proposed that the precipitate-free zone is anodic to the matrix in a stress corrosion environment [154].

Table 14—The Availability of Wavelength Dispersive Spectrometer for Use on Scanning Electron Microscope

SEM Manufacturer and Model	Guaranteed Resolution ($\text{\AA}$)	No. Of Spectro- meters sf=semi- focus ff=full focus	No. of Crystals in Each Spectro- meter	Take off Angle in Degrees	Light Micro- scope Avail- able and Mag.	Normal Beam Incident Possible
AMR/900	150	2ff	2	30 ¹	yes-300X	yes
ARL/SEM	200	2ff	2	52.5 ¹	yes-560X	yes
Cambridge/S4	150	2sf	4	0-70	no	no
CAMECA	200	2ff	4	45	yes-70X	no
Coates & Walter ² /100	250	4				
ETEC	200	2ff	4	45 ¹	yes-600X	yes
Hitachi/HSM-2	150	1ff	3	20 ¹	no	yes
JEOL/JSM-U3	100	2ff	3	30 ¹	yes-560X	yes
MAC/EBS-21	150	1ff	1	0-90	no	no
Ultrascan/SM3	75-125	2fforsf ³	2	30 ¹	no	yes ⁵

1) At normal incidence. 2) has field emission gun. 3) two spectrometers either fully or semi-focusing of a combination of either. 4) WDS not presently available with this unit. 5) only possible with fully focusing spectrometers.

We were unable to detect any depletion in bulk samples or thin films using an EPA while crossing to boundary at a shallow angle ($\sim 10^\circ$). We were also unable to detect depletion in a thin film using an EPA equipped with a TEM attachment and encountered difficulties because of sample thickness variation from one side of the boundary to the other. Unwin et al [155] did detect some depletion in a bulk sample, but because the work was done at 25 kV the spatial resolution would not have been better than $4\ \mu\text{m}$. Shastry and Judd [156] also detected a slight depletion in bulk samples (air cooled and aged at 200 C for 4 h) of about 0.4 percent Zn and 0.2 percent Mg from the composition in the surrounding matrix, which contained 6.3 percent Zn and 2.6 percent Mg. The same authors observed slight Zn and Mg enrichment at the boundaries of alloys brine quenched and aged at 27 C, but these measurements indicated enrichments extending over $100\ \mu\text{m}$. This work was also carried out at 25 kV.

Duncumb has discussed [157] the work of Jacobs [158] using EMMA 4 in which the Zn/Al counting rate ratio in an Al-26 Zn alloy dropped from 0.95 in the matrix to 0.55 at the boundary when a 2000-Å-thick film was examined at 100 kV. With the 1000-Å electron beam it was actually possible to pass between precipitate particles in the boundary.

An instrument such as the EMMA 4 is complimentary to an EPA and is capable of easily solving specific problems that would be solved, at best, with great difficulty using other techniques. The long-standing problem of asbestos particle-type identification [159] in lung tissue would appear to be ideally suited for the EMMA 4. It would also be desirable to confirm with the EMMA 4 the work of Bercovici et al [160], who reported a substantial enhancement of solute concentration at grain boundaries in Zn-0.1 Cd alloys. The enhancement increased with increasing annealing temperatures and cooling rates and was detected when atomic absorption spectrophotometry was used to analyze material selectively removed from the grain boundaries by etching.

A less satisfactory, but often workable, solution to the need for a TEM-EPA combination is the addition of X-ray spectrometers to existing TEMs. The advent of high sensitivity EDS makes this more feasible now than in the past because of the low intensities expected from thin films. Some TEMs were equipped in 1963 with a gas proportional detector but the resolution inadequacy limited their use. Bender and Duff [161] have reported on installing an EDS on a TEM and predict low mass sensitivities. The major limita-

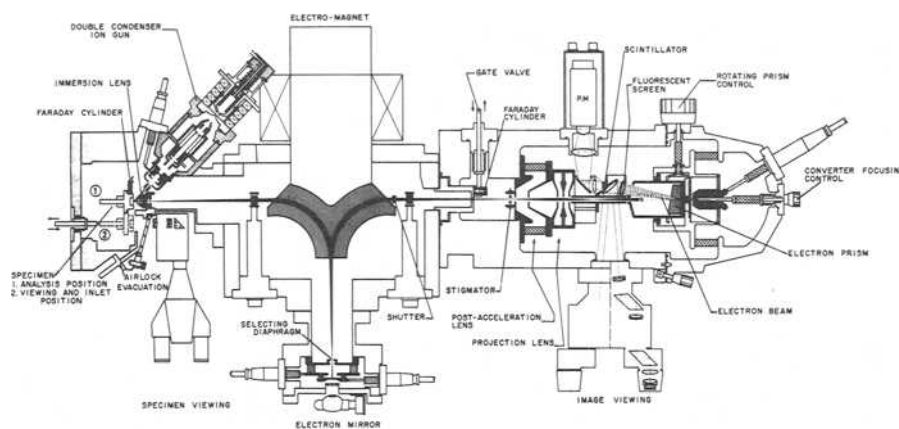


Fig. 31—A schematic diagram of the ion mass analyzer manufactured by CAMECA, courtesy of Janichewski [184].

tion of such a system is the fact that the minimum beam size attainable in most existing TEMs is limited to the range from 1 to $2\ \mu\text{m}$, thus limiting the spatial resolution.

Auger Electron Spectroscopy (AES)

General Description/ An excited atom with a vacancy in an inner shell can return to its ground state or some lower energy state by the emission of a characteristic X-ray photon or of an electron known as an Auger electron, after P. Auger [162] who first observed this radiation-less emission. In the Auger effect the atom is left with two vacancies, and an Auger electron is released with an energy E_{Auger} equal to $E_X - E_{YZ} - E'_X$, where E_X is the total energy of an atom with a vacancy in an inner X shell, E_{YZ} is the total energy of an atom with two vacancies, one in the Y shell and one in the Z shell (Y and Z refer to two outer shells), and E'_X is the energy the ejected electron must expend to escape the atom. For the specific case of an KL_1L_2 Auger electron (vacancies in the L_1 and L_2 shells), the Auger electron energy will be $E_{\text{KL}_1\text{L}_2} = E_K - E_{\text{L}_1\text{L}_2} - E'_K$. As in the case of characteristic X-rays, the energy of the Auger electron depends on the parent atom and, therefore, can be used for atomic identification. The reader is directed to Refs 163 and 164 for comprehensive reviews of AES.

Analysis of Low Atomic Number Elements/ Auger electrons offer some distinct advantages over X-ray photons in the analysis of light elements. The ratio of the number of photons generated to the number of inner shell excitations is the fluorescence yield ω . For atomic numbers below 32 the fluorescence yield is less than the Auger electron yield, which is the ratio of the number of Auger electrons generated to the number of inner shell excitations (Auger yield + $\omega = 1$). The analysis of low

Z elements is hindered by the low fluorescence yield, by the use of pseudocrystals with poor resolution and consequent interference problems, and by the absorption of long wavelength radiation. Auger electrons, on the other hand, are plentiful at low Zs. The peak spacing in the Auger spectrum permits low Z elements (Li to Cl) to be easily resolved from each other by existing electron velocity analyzers [165], and low energy electrons are efficiently and easily detected using scintillation counting techniques. In these analyzers the Auger electron current ($10^{-12}\ \text{A}$) is extracted from the energy distribution of backscattered electrons ($10^{-9}\ \text{A}$) by electronic differentiation of the energy distribution [166,167].

Spatial Resolution and Surface Analysis/ It was shown in Fig. 12 that only a small amount of electron scattering occurs near the target surface; thus, in this region the diameter of the excited volume is approximately equal to the beam diameter. In AES, Auger electrons with energies ranging from 50 to 1000 eV are generally used. Since low energy electrons are easily absorbed by the target, only electrons generated close to the surface (usually within 10 Å) escape the material and are detected. This results in an active Auger volume a few angstroms deep and not significantly wider than the beam size and provides the potential for surface analysis with a spatial resolution near 200 Å. This resolution potential has not yet been completely achieved, because the need for high beam currents in order to generate a detectable Auger electron signal results in an increased beam diameter in present-day instruments. The detectability limits are in the 10 to 1000-ppm range for most elements.

MacDonald et al [168] have carried out an Auger analysis in a SEM operated at 15 kV with a beam diameter of $0.5\ \mu\text{m}$ and a beam current of 100 nA. They measured

a variable Sb/Fe ratio on the fracture surface of a Fe-1.5Sb alloy which had been fractured in the SEM. Viswanathan [169] analyzed the prior austenitic grain boundaries in embrittled and nonembrittled Ni-Cr-C-P steel and found P segregation within 10 Å of the boundary and Ni segregation within 50 Å of the boundary in embrittled materials. His work was done with an ion gun to remove successive layers of material from a fractured surface. Additional applications can be found in Refs 167 and 170-174.

Incorporation into Other Instruments/ Major problems in AES or any other surface analysis are those of surface contamination [174] and the relation of surface properties to bulk properties. Contaminants on the specimen surface, the absorption of residual gases, and instrumental C contamination can complicate the Auger electron spectrum. Consequently, Auger analysis is best carried out under a vacuum of 10^{-9} torr or better; and vacuum improvements are needed in commercial instruments if effective AES-SEM-EPA combinations are to materialize. A broad capability instrument with an ultimate vacuum of 10^{-9} – 10^{-11} torr cannot be easily built, but some commercial manufacturers have developed prototypes of such an instrument. These prototypes have either LaB₆ or field emission guns, which provide considerably higher

beam currents in a small (200 Å) electron beam.

An ion gun for use in conjunction with an AES is an intriguing combination which provides in-depth resolution capabilities approaching 5 Å and is based on controlled erosion followed by AES analysis. Such a combination incorporated into an SEM or EPA with a high brightness source could provide high spatial resolution in addition to true surface analysis. The possibility of quantitative analysis is not remote. The cost of an instrument consisting of a LaB₆ or field emission gun, an ion etching gun, AES, EPA or SEM, EDS, and WDS depends to a large extent on the cost of incorporating such accessories into a 10^{-9} torr environment.

The Ion Mass Analyzer and Ion Microprobe Analyzer

Exciting new vistas of scanning microanalysis have recently appeared as a result of the commercial availability of instruments which bombard a specimen with a beam of high energy primary ions. These create an emission of secondary ions which are then analyzed by a mass spectrometer. This simple statement conceals some extremely complex and highly sophisticated instrumentation, the detailed description of which lies outside the scope of this report and can be found in Ref 175-183. The discussion here will be primarily con-

fined to those applications which illustrate how the technique fits into the overall scheme of microanalysis.

The Instruments/ The instruments making possible microanalysis by secondary ion emission are basically of two types: ion microscopes and scanning ion probes. They have been identified by several names: ion mass analyzer (IMA), ion microprobe analyzer, ion microprobe mass analyzer (IMMA), imaging mass analyzer, secondary ion emission microanalyzer, ion emission microscope, imaging mass spectrometer, ion microscope, ion probe, ion microanalyzer, and direct imaging mass analyzer (DIMA). Since a universally accepted nametag has yet to evolve, we will use IMA to denote either the ion mass analyzer or the ion microprobe analyzer.

The Ion Mass Analyzer-Ion Microscope—The ion mass analyzer developed by Castaing and Slozdzian, is discussed in the thesis by Slozdzian [178] and in the paper by Castaing and Slozdzian [177]. Note that once again Rammond Castaing has played a predominant role in the development of an extraordinary microanalytical device of a different nature than the EPA. Improvements in this instrument (Fig. 31) have been described by Ruberol et al [182, 183]. Primary ions are produced in a duoplasmatron gun, accelerated and focused at the specimen surface by a double condenser lens to a diameter of 20 to 400 μm, but usually about 250 μm. The primary ions most often used are Ar⁺, O⁺, and O₂⁺.

While most atoms leaving the specimen are neutral, a measurable fraction are ionized. The secondary ions, characteristic of the elements in the specimen, are accelerated by an immersion lens which accelerates and focuses the total ion beam for entry into the mass spectrometer portion of the instrument. (Focusing allows use of circular apertures, which results in high transmission.) The mass analyzer system consists of a magnetic prism, an electrostatic mirror, and another magnetic prism. The first magnetic prism separates the total ion beam (composite elementary image) on the basis of m/e ratio, the mirror provides energy filtering and directs the ion beam back into the second magnetic prism, where a second deflection occurs and the ions are directed toward an image converter. Here the ions are accelerated and impinge upon a cathode where they generate an equivalent electron image. These electrons are, in turn, accelerated and impinge upon a fluorescent screen, where they can be observed visually at about $\times 400$. This electron image can also be photographed on film located in the converter vacuum enclosure.

When this total image is observed or

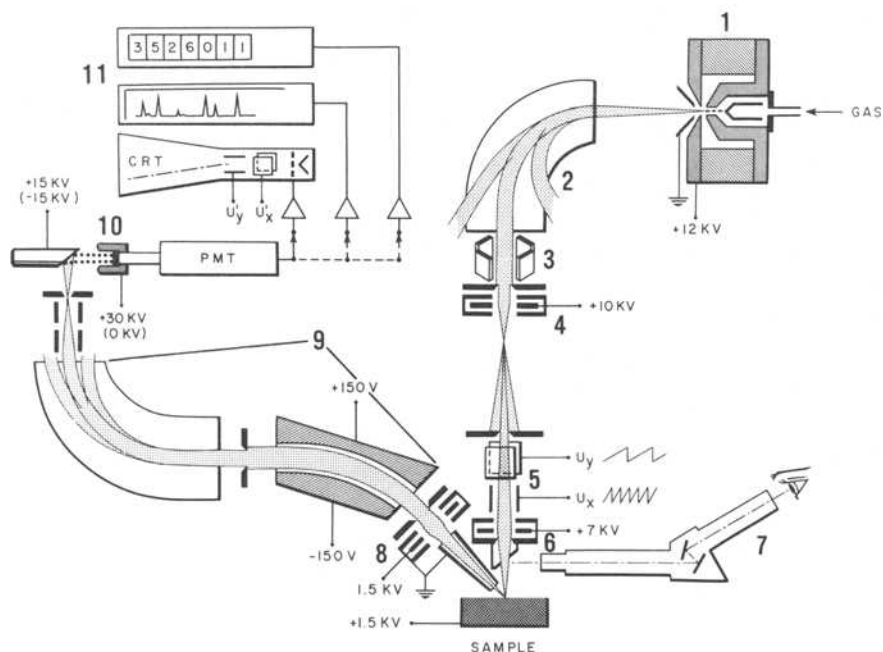


Fig. 32—A schematic diagram of the Ion microprobe mass analyzer (IMMA) manufactured by ARL. (1) Duoplasmatron ion gun serving as primary ion source; (2) primary magnet for mass separation and primary beam purification; (3) deflection plates; (4) electrostatic condenser lens; (5) deflection plates for beam sweep; (6) electrostatic objective lens; (7) light optical microscope; (8) secondary ion extraction lens; (9) mass spectrometer; (10) ion detector and photomultiplier tube; (11) readout capabilities. Schematic courtesy of Andersen [181].

**Table 15—Comparative Performance and Characteristics for the
Ion Mass Analyzer and the Electron Probe Analyzer**

<u>Characteristic</u>	<u>EPA</u>	<u>IMA</u>
Bombarding particle	electrons	primary ions (+ or -)
Analyzed	photons	secondary ions (+ or-)
Spatial resolution in image (μ)	<1	1
Quantitative resolution (μ)	1-5	>5
Image magnification	300-7000X	400-7000X ¹
Optical observation during bombardment	yes	yes ²
Image observed on	CRT	fluorescent screen or CRT
Image exposure times (sec)	5-1800	0.001-60
In-depth analysis	difficult	easy
In-depth resolution	0.1-5 μ	50-200 $\text{\AA}$ ⁰
Erosion rate ($\text{\AA}/\text{sec}$)	0	10-1000
Destructive	usually not	always
Size of bombarded area (μ)	beam diameter	2-3 as probe 250 as microscope
Vacuum (Torr)	10^{-4} - 10^{-5}	10^{-7} - 10^{-8}
Mass resolution $M/\Delta M$	n.a.	300-1000
Sample preparation	metallographic	metallographic
Cost (\$1000)	60-120	225-270
Isotopes detected	no	yes
Analysis of z	≥ 4	all ³
Sensitivity for $z < 10$	poor	high ³
Detectability	50-1000 ppm	10ppb to 100ppm
Mass sensitivity (g)	10^{-15} to 10^{-16}	10^{-18} to 10^{-19}
Quantitative accuracy ($\Delta C/C$)	1-3%	not established ⁴ on a broad basis

1)the higher magnification is possible when using a CRT;2)yes for the ion microprobe but no for the ion microscope;3)however, the sensitivity for some elements is poor, e.g. He and Hg;4)Andersen has successfully analyzed silicates(185).

photographed, the instrument functions as an ion microscope displaying the distribution of any selected isotope in the bombarded area of 250 μm . In the imaging mode a particular isotope distribution is continuously observed as the specimen is moved beneath the beam. Because the collection efficiency of the immersion lens and the transmission efficiency of the mass spectrometer are high, these chemical distribution maps can be recorded in milliseconds to a few seconds. By inserting a small aperture into the image plane, the ion current coming only from a selected area of the bombarded area of the specimen can be measured. The smallest useful diameter is determined by the inherent spatial resolution, which can approach 1 μm . In this mode, after passing

through the aperture, the electron beam impinges upon a scintillator-photomultiplier.

The selected area mode of mass spectrometer analysis requires about 1 to 3 min, depending on the desired sensitivity, for a complete mass spectral scan for all the elements in the periodic table. The secondary ions coming from the sides of the eroded region (often called a crater) are not included in an analysis operated in the selected area mode, which is important during in-depth analysis. In addition, the secondary ions generated at the edge of the primary beam are eliminated by the mechanical aperture. In this region (gaussian tails of the primary beam) the ion bombardment may fall off to the level at which the rate of arrival of the primary ions cannot compete effectively with that

of the impinging residual ambient atoms (for example, H_2O) and chemical reaction may occur. When a large aperture is used, the instrument operates as a high sensitivity mass spectrometer examining an area of about 125 μm (100 to 250 μm depending on aperture) on the specimen surface. When the primary beam is focused to 20 μm the erosion is held to a minimum and the instrument functions as an ion probe.

The Ion Microprobe Analyzer—The ion microprobe analyzer shown schematically in Fig. 32 is the ion probe designed by Liebl [176] and has been thoroughly discussed by Andersen et al [185–190]. Here a duoplasmatron gun produces the primary ions, which are accelerated and then purified by passage through a mass prism that permits primary ion bombardment with a selected ion species. The primary beam is focused electrostatically to a fine beam at the specimen surface (2 to 3 μm presently). Secondary ions are accelerated into a mass spectrometer and the mass-resolved secondary exciting ions impinge upon the conversion electrode of a Daly-type detector. Isotope images are formed (tuned to a particular mass) by sweeping the ion beam in synchronization with the beam of a cathode ray tube, providing magnifications of up to 7000. In the static mode the mass spectrum can be recorded by sweeping the magnetic field, or at a fixed mass the variation in ion intensity can be measured.

One manufacturer [192] has recently announced the availability of an accessory to their spark source mass spectrometers which should allow them to function as ion microprobe analyzers. With this instrument all masses can be recorded simultaneously on a photoplate, thus overcoming some of the problems associated with material erosion. When not using the apparatus as an ion microprobe the analyst has at his disposal a high quality, spark source mass spectrometer. The primary ion beam can be focused to a 5- μm diameter.

IMA versus EPA: Applications/ The ion mass analyzer offers several complementary and some competitive features when compared with an EPA and the two are compared in Table 15. Because of the intense interaction between ions and solids, the penetration is low and the analysis is restricted to a surface analysis; and, while the resolution in depth depends on the specimen and isotope of interest, it is expected to be in the range of 50 to 200 Å. The in-depth resolution will improve as the secondary ionization efficiency and isotope concentration increase, because less material is required to give a specific ion intensity. The ion yield can often be enhanced by using a reactive gas (such as oxygen), which presumably generates an

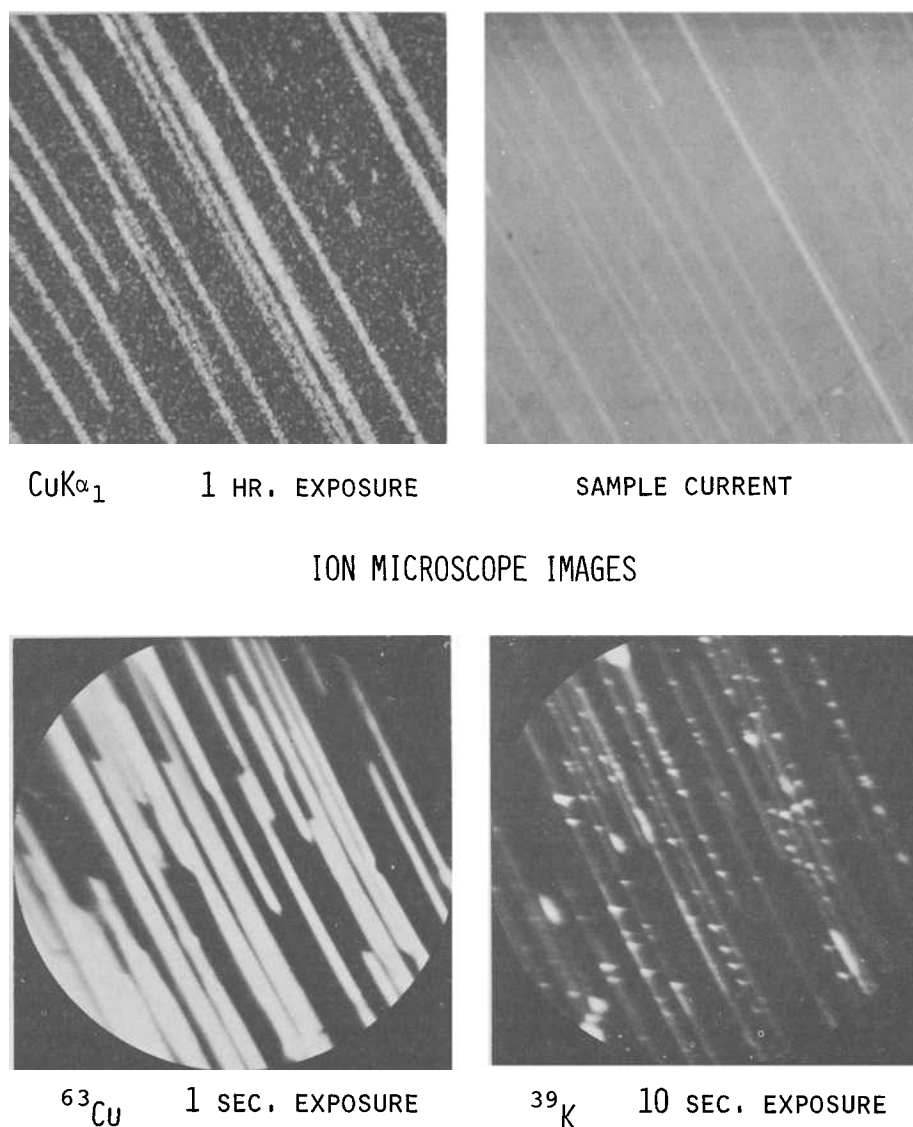


Fig. 33—A comparison of images obtained on the IMA and the EPA. The upper images are X-ray and specimen current images from an EPA and the lower images are isotopic images from a CAMECA IMA. All images are at a magnification of approximately 400. It was not possible to detect K with the EPA. Photographs courtesy of Lewis [194].

oxide with ionic bonding at the surface. Sputtered material has a higher emitted ion/neutral atom ratio in cases of ionic bonding.

The most remarkable applications of the instrument to date have been in the area of in-depth analysis [193], particularly in semiconducting materials. In this type of work the mass spectrometer is set for the desired mass and the ion current is recorded as a function of time for a presumably known erosion rate. This erosion allows successive underlying layers to be exposed and analyzed. The erosion rate depends on the mass, energy, and intensity of the bombarding ion, the primary ion current, and the nature of the specimen. We have found a highly concentrated layer of Be about 100 Å below the surface of Mg alloy die castings. Lewis et al [193] discovered high concentrations of Si (1 atomic percent) and K (~0.1 atomic percent) 6 μm beneath the surface of an epitaxial layer of GaAs on bulk GaAs, which corresponded to the film substrate interface. The concentration was restricted to a depth of less than 1 μm. In-depth resolution for a given spatial resolution will depend upon the needed precision, the secondary ion yield and the isotopic concentration. Extreme care in experimental design must be exercised because, once such an experiment is performed, erosion prevents it from being repeated in the same area.

All elements can be analyzed, including H, He, Li, and Be, however the sensitivity for He is poor. H and He, of course, cannot be analyzed with an EPA because they lack outer shell electrons; Li radiation (240 Å) is extremely soft; and Be, presently, can only be analyzed in EPAs when present in relatively high concentrations. Just as important is the high sensitivity of the IMA for elements such as B, O, and F, which are neither easily nor accurately analyzed with the EPA. Molecular species can be detected with the IMA. The sensitivity of the IMA is on the order of that attainable with a mass spectrometer and is expected to lie in the range of 1 ppb to 10 ppm. The lack of a continuous background, so troublesome in the EPA and more so in an EDS, allows this sensitivity and suggests an expected mass sensitivity on the order of 10^{-15} to 10^{-19} g.

Because the IMA operates as a microscope, it is often possible to obtain images almost instantaneously, as compared to the minutes required in an EPA, which is indeed fortunate in view of the continuous erosion. The relative speed of the photographic image formation is illustrated in Fig. 33 [194], where Cu striations in CdS are obtained in 1 and 3600-s exposures for the IMA and EPA, respectively. The K was not observable in the EPA.

Table 16—Past and Anticipated Applications of the Ion Mass Analyzer

<u>High resolution (100 Å) in depth diffusion profiles</u>
(a) ^{11}B in single crystal Si (182)
(b) Impurities at epitaxial GaAs film-substrate interface (193)
(c) 2 ppm Ni in an 100 Å thick surface layer on an integrated circuit (195)
<u>Light element analysis (H-F)</u>
(a) Be in cast Al alloy (196)
(b) Be in Mg die castings*
(c) Li in Mg-Li-In alloys*
(d) H in Mg-Zr alloy*
(e) H, B and Na in granite (182)
<u>Self diffusion with non-radioactive isotopes</u>
(a) ^{18}O diffusion in UO_2 (197)
<u>Secondary ion emission phenomena</u>
(a) Effects of chemical bonding on emission
(b) Orientation, trace impurity levels, temperature, etc.
<u>Trace analysis</u>
(a) Na in red blood cells (181)
(b) Impurities in epitaxial GaAs - 2 ppm Na; 0.2 ppm Al; 2 ppm K; 0.2 ppm Ca; 1 ppm Fe; also Mn, Si and Ti (196)
(c) 40 ± 10 ppb P in a phosphated glass layer on an integrated circuit (195)
<u>Isotopic segregation and ratios</u>
(a) Pb isotopic ratios in Uraminite (196)
(b) ^{206}Pb , ^{207}Pb and ^{208}Pb in Pitchblend (182)
<u>Surface analysis</u>
(a) Oxidation, corrosion, passivation, catalysis, chemisorption
(b) Oxygen on a Mg surface (177)
(c) Deposited films, coatings
(d) Measurement of film thickness
<u>Three-dimensional chemistry</u>
(a) the correlation of photographic images with depth

*present investigation

The high sensitivity should be particularly intriguing to the biologist who has been struggling with the EPA. The detectability limits in the EPA of the biologically important elements are on the order of 500 ppm, which represents a borderline situation in many cases. The move into the ppb range should be welcome and exciting. A laboratory equipped with an SEM, an EPA, and an IMA would appear to offer a staggering potential in the areas of biological and materials research, notwithstanding the \$400,000 to \$500,000 required to establish such a facility. It would certainly be advantageous to have an ion etching capability in the EPA. While isotopic analysis will be most useful in geological applications and in self-diffusion studies, the ability to detect isotopes in low concentrations in biological specimens holds great promise in the area of nuclear

medicine. Thermal destruction of tissue should be less of a problem than with the EPA. Some areas of application of the IMA are listed in Table 16.

Expected Problem Areas/ There are, of course, problem areas, particularly since the IMA is new and only a few installations exist. There are eight IMAs operating in the United States today, ten in Europe, and three in the U.S.S.R. Quantitative analysis on a broad basis is certainly a distant, but not improbable, prospect. Andersen [185] has reported on the successful analyses of some silicates. The process of secondary ion emission in complex alloys promises to be a most interesting subject. Chemical bonding, specimen conductivity, intra-element effects, elemental concentrations, the physics of ionization in solids, crystallographic orientation, and the nature and energy of the primary ion all affect the

Table 17—Some Identification Techniques and Parameters-Generalized (from Henry and Blosser, Ref. 199)

Technique	Determined	Simultaneously	Precision	Lower limit	Amount of	Useful range	Approximate costs	Mass sensitivity ²
Emission Spectrography	Metallic elements	Yes	3-10	Yes	20 mg	Lower limit to 5%	\$25 to \$50 3-10 elements	11
X-ray Spectrography	Elements Atomic No. >11 (Na)	Yes	1-5	No	10-1000 ppm	Lower limit to 5	\$5 per element	7
Spark Mass Spectrography	All elements	Yes	10-50 1-10	Partial	0.003-0.3 ppm	Lower limit to 1%	\$75 to \$200 \$75 to \$200	12
Electron Microprobe	Elements >14	Yes	1-5	No	100-1000 ppm	Lower limit to major compound	\$75 to \$200	14-16
X-ray Diffraction	Crystal structure Phases, compounds	Yes	5-10	No	1-5%	Lower limit to major compound	\$50 to \$200	10
Metallography	Visual & photographic	Yes	1-1000x magnification	No	>1 μ^2	1 μ resolution	\$25 to \$150	
Light Microscopy	Visual & photographic	Yes	1-1000x magnification	No	>1 μ^2	1 μ resolution	\$25 to \$100	
Electron Microscopy	Visual & photographic	Yes	Partial	Partial	1000-10000x magnification	10-100000 $\times$	\$50 to \$300	
Scanning Electron Microscopy	Visual & photographic	Yes	No	No	15-50000x magnification	150 $\times$ -cm ²	\$50 to \$300	12-16 EDS
Activation Analysis	Most elements-some chemical separation	No	1-10	Yes and No	0.001 to 100 ppm	Lower limit to 5%	Too variable to estimate	11
Chemical	Most elements	No	1-5	Yes	10 to 100 ppm	Lower limit to 50%	\$5 to \$35 per element	9
Chemical Color Stain, Spot Test, etc	Most elements	No	1-5	Yes	0.01 to 10 ppm	Lower limit to 1%	\$5 to \$35 per element	
Atomic Absorption	Up to 50 elements	No	1-5	Yes	0.1-100 ppm in solution	Lower limit to 10%	\$5 to \$10 per element	10
Flame Emission	Alkali and alkaline earth elements	No	1-5	Yes	0.1-10 ppm in solution	Lower limit to 10%	\$5 to \$10 per element	11
Vacuum Fusion	O, H, N	Yes	10	Yes	0.1-10 ppm	Lower limit to 1%	\$45 for O, H, & N	7
Ion Mass Analyzer	All elements	No	?	Yes	0.1-100 ppm	Lower limit to major compound	\$50 to \$500	18-19
Laser Microprobe	Same as emission spec	Yes	10	Yes	1-10 ppm	Lower limit to 5%	\$20 to \$50	8
Auger Spectroscopy	Elements >13	Yes	?	No	10-800 ppm	Lower limit to major compound	\$75 to \$250	

1) amount of sample consumed or examined for best detection; 2) mass sensitivity in 10⁻⁸ grams with x indicated; 3) not yet established

secondary emission and will lead to complexity in establishing an emission concentration relationship applicable to a broad spectrum of materials.

Interferences in the EPA (WDS) are uncommon. In the IMA the present mass resolution (300) is such that the problem is usually not serious. The vacuum requirement of 10⁻⁹ torr, essential if the best sensitivity is to be attained, may lead to maintenance problems caused by the continued erosion of a variety of specimen types. The preferential ionization of different crystallographic orientations could lead to significant interpretive problems in multiphase materials. In single crystalline semiconductors this is not a problem. The presence of organic materials in the system (mounting materials, substrates, impregnants, biological matrices) will lead to peaks (O⁺, O₂⁺, O⁻, O₂⁻, C₂H⁺, C₂H₂⁺, NO⁻, etc.) that could interfere with the analysis.

The predicted lower sensitivities (in the ppb range) have not been experimentally achieved yet and are, for the most part, based on calculations using known erosion rates and secondary ion yields, which neglects such problems as isotope interferences and impurities in the primary ion beam. Nishimura and Okano [198] have constructed a simple IMA with a 250- μ m primary ion beam and have measured detectable limits of 5 ppm B in Si and 1 ppm Cr in Fe. Bayard [195] has used an ion probe to measure low concentrations of several elements in Si.

Nonconductive specimens are made conductive by the deposition or use of a conductive grid which is also etched by the ion beam; however, the specimen need not be conductive if a negative primary beam is used. Because erosion rates are not usually well known, it will often be necessary to study the ion bombarded surface microscopically after the analysis. An SEM will provide the best results in most cases. When operating in the microscope mode, the analyzed area is kept clean by the large primary beam. There is no redeposition of eroded debris in the area being analyzed and the walls of the crater are far enough removed to not contribute material to the analyzed region.

Comparison of Analytical Techniques

Throughout this report the high mass sensitivity of various techniques has been mentioned. At this point we would like to briefly compare a wide range of analytical techniques.

Table 17, taken from a report by Henry and Blosser [199], is a fine summary of the different analytical techniques. We have added the last column of mass sensitivities indicating the minimum number of grams

of material of the analyzed element that must be present in the specimen to afford detection; most of these values are from Marton [200]. The ion mass analyzer, laser probe, and Auger electron spectroscopy have also been added. Any such tabulation must, of course, be approximate, since the capability of any technique often depends upon the state of the specimen, the analyzed element, the matrix, etc., and an ingenious analyst can often improve performance by one order of magnitude.

The EPA is seen to be capable of non-destructively analyzing all elements except H, He, and Li, with a mass sensitivity second only to the IMA and a spatial resolution second to none (the SEM-EDS is an exception in certain cases) over the broadest range of compositions (50 ppm—100 percent), usually with high accuracy (1 to 3 percent of the amount present), at a high cost, and after a long analysis time. Margoshes [201], who succinctly reviewed techniques capable of providing microanalyses of volumes of materials ranging in diameter from 1 to 100 μm , found that the EPA provided the best spatial resolution at the highest capital expenditure for equipment.

The need for highly sophisticated microanalytical techniques is illustrated by the enormous interest in human health and ecological problems today. The typical sizes of several organic materials are as follows: viruses, 100 $\text{\AA}$; bacteria, 5 μm ; red blood cells, 7 μm ; white blood cells, 14 μm ; intercellular constituents excluding the nucleus, 0.4 to 8 μm ; the cell nucleus, 4 to 50 μm ; asbestos bodies, 0.2 to 40 μm ; automobile exhaust particulate matter, 0.1 to 3 μm ; gas turbine exhaust particulate matter, 4 to 6 μm .

Automated Instruments

For many years investigators have been writing computer programs for data reduction and correction purposes. Data reduction, as applied to the EPA (or SEM-EDS), refers to the correction of measured peak intensities for deadtime, background, and drift prior to the calculation of the measured concentration or probe ratio k . Versatile programs also perform statistical analyses of the measured intensities. The correction programs convert the measured concentration to the actual chemical composition. Of the 40 available correction programs, 25 contain data reduction capability [202].

This represents the past use of the computer in conjunction with the EPA. What about the present and future? The defined areas of interest are the ability to have compositions calculated directly from the recorded digital data and computer control

of the instrument. The former was accomplished in the past by first placing the scaler output data on punch paper tape and then having the data processed using one of the several data reduction programs available that accept a punch paper tape input [202]. It is more useful to handle the data directly through an interface coupled directly to a small, dedicated computer.

Dedicated Computers/ The use of dedicated computers is gaining rapidly in popularity, because (1) it is neither economical nor efficient to tie in directly with a larger computer installation; (2) the cost of small computers is surprisingly low; (3) the dedicated computer is always available for immediate use; and (4) even with limited core storage, investigators are devising techniques that enable a small computer to provide probe control, data reduction, and correction. For example, Chambers [203] has used a PDP8/I and a 256K-word random access disk to meet the core storage requirements often encountered in complete correction programs.

At the last national meeting of the EPASA in July 1970, three reports were presented on computer controlled EPAs: (1) Eichen, Kunz, and Matthews [204] working with an MAC probe, (2) Wolf and Saffir [205] working with an MAC probe; and, (3) Chambers [203] working with an ARL probe. In addition, Bayard [142] has reported on his experiences over the last three years with an ARL probe interfaced with a computer. These investigators have demonstrated that with a dedicated computer it is possible to control (select a value or rate and start, stop, and move, that is, position at a selected value) the electron beam, specimen stage, and spectrometers. Work is being done on controlling such parameters as the base line and window voltages of the PHA, timer and scaler values, electron beam current, linear amplifier gain, and detector anode voltage.

The more difficult problems of focusing and maintaining a focused electron beam, altering the acceleration potential while maintaining a focused condition, monitoring and correcting for various instrumental instabilities (current, spectrometer, and voltage drift), and accurate optimization of the spectral peak intensity have not been solved but will be in the future. The McCrone [142] system stops the probe operation when a loss of X-ray intensity or beam current is encountered; it also periodically checks the various power supplies. Likewise, water pressure, gas flow, column vacuum, spectrometer vacuum, room temperature, humidity, and line voltages could be monitored as a safety precaution and to ensure that operating conditions were ideal. Eichen et al [204] and Chambers [203] have demonstrated

the ability to do on-line quantitative analysis with a dedicated computer.

Areas of Application/ The many advantages of a dedicated computer system are certainly apparent. It greatly facilitates any repetitive-type analysis: measurements of diffusion profiles in hundreds of finite steps; homogeneity studies; the generation of concentration maps; multiposition multielement analyses in complex materials (analyzing grains in geological samples); and the analysis of particulate material where large numbers of similar particles are encountered as in air pollution samples, auto exhaust particulates, and blood smears [206]. The possibility of leaving the instrument unattended during these valuable but boring and time consuming analyses in many cases can justify resorting to a computerized instrument.

One valuable aspect of a computer controlled probe is the access to immediate statistical evaluation of accumulated data. By isolating specimen and instrumental variations, it will be possible to prevent the collection of data under less than optimum conditions. Rapid statistical evaluation, available in 18 of the 40 published programs, and data rejection, in 2 of the 40 programs, prior to computer processing for conversion to composition will be extremely useful. While such a capability will not improve the accuracy of quantitative analysis, it will increase the amount performed. The pitfall here lies in the indiscriminant use of statistical parameters, without attempts to identify and understand the causes for the observed variations and in particular to ascribe instrumental difficulties to variations in the specimen. When instrumental problems are understood, a continuous statistical data evaluation can be of great assistance.

There are also the obvious advantages in the avoidance of human error in data tabulation, transmittal, reduction, computation, and reporting, in addition to more rapid analyses. Bayard [142] reports analyzing 15,000 specimens with the McCrone system in three years. On the basis of 8 h of operation per day, that corresponds to one specimen every 25 min—a remarkable feat for an EPA. Eichen and Kunz [207] are attempting to replace the MCA used with the EDS by a dedicated computer.

Quantitative Metallography (QM)/ The computer can also be used to perform qualitative and quantitative metallography (stereometric analysis) of the type described by Dorfler [208]. Stereometric analysis is the quantitative characterization of three-dimensional structures by the measurements of plane surfaces, either sections or projections. The distribution of phases can be determined, giving information concerning their number, size, shape, area, weight fraction, volume frac-

tion, and composition. The superposition of the distribution in composition on the others, which have been determined optically for years, represents one of the most useful applications of an EPA (or SEM-EDS-WDS system). The possibilities appear to be limited only by the investigator's ability to generate the necessary software.

Commercially available devices for use on the EPA have been described [209], [210], and Ogilvie et al [211] have described a system for use with the SEM. Dorfler and Russ [212] performed a QM analysis with an EDS and a phase integrator (based on a window-discriminator concept) in a SEM and obtained information on the volume fraction, mean particle size, surface area, particle size distribution, and particles per unit area.

In quantitative metallography one problem area, from the point of view of complete computer control, is the correlation of any measured distribution with the various images—X-ray, specimen current, backscattered electron, secondary electron, and optical. Most EPAs do not provide high quality, high magnification optical images, and an ultimate aim of quantitative metallography is the correlation of the optical appearance of the phase (brightness, color, shape, size) with the composition. On the other hand, secondary electron images are of high quality. The selection of the optimum analyzing conditions (signals to be used, scan speed, number of lines, etc.) is a problem in some

cases. X-ray intensity is the most useful signal for establishing compositional distributions, since specimen current, back-scattered current, and secondary electron current often do not provide adequate discrimination and are strongly dependent upon the condition of the specimen's surface. Electron signals are preferred for size and shape measurements because of the better resolution they allow.

What Is Available and Its Expected Cost/ The cost of a complete computer capability encompassing the following items is presently unknown: (1) control of spectrometer, beam, and specimen position, (2) other control features (alignment, etc.), (3) monitoring functions, (4) statistical evaluation, (5) quantitative metallography, (6) computer processing of images, (7) repetitive analysis, (8) data reduction, (9) chemical analyses, and (10) data presentation. Including a small computer, the computer interface and the driving devices, the control of the spectrometer, beam, and stage positions can be accomplished at a cost of about \$13,000 per spectrometer.

At present, we know of two suppliers of equipment specifically directed at EPA automation. One manufacturer [213] provides a system that can reposition the spectrometer to within ± 0.0001 Å, position the beam anywhere within a 1000 by 1000-point matrix, move rapidly to and slowly across a peak location, count whenever a signal above a preselected value is encountered, and analyze 1000 points

along a line. Another manufacturer [142] has developed a useful stage concept where the specimen holder is examined optically by the interested investigator (biologist, geologist, metallurgist, etc.) in a stage identical to the one used in the EPA. The coordinates of areas of interest are recorded, the specimen is transferred to the EPA, fiducial marks on the specimen holder are located, the coordinates are adjusted accordingly, and automated analysis proceeds.

Is Automation Advisable? Electron probe automation is new, exciting, useful, and in some applications necessary; however, the EPA has, to a large extent been used as a highly sophisticated research tool. It will no doubt continue to be used in this manner, and many outstanding contributions can be expected from EPAs lacking automation. Some of the best research performed with EPAs is coming from laboratories using vintage instruments. The added hardware required in automation will certainly lead to additional downtime as a result of component failure. Hopefully, self-diagnosis will be possible. One would also like to have the option of returning to full manual operation. Most important is the fact that many problems do not lend themselves to a computerized approach. The analyses of thin films, corrosion products, specimen edges, intracellular components, interfaces, specimens of nonuniform density, phases containing volatile constituents, magnetic materials, cathodoluminescence effects, and fractured and rolled surfaces often do not have a defined endpoint and, thus, the analyses cannot be programmed.

When one considers the number of answers to complex problems that have appeared as the analyst more or less stumbled through the analysis, it seems wise to consider carefully the need to turn to total automation. Still it appears clear that future-generation instruments will have to be, and justifiably so, engineered for automation with different packages available as options. It seems safe to predict that most EPAs sold in the seventies will have a dedicated computer as an accessory.

Applications

Before embarking upon a detailed discussion of the complexities of experimental measurement and quantitative analysis, we would like to discuss some of the meaningful results that have been achieved in the past.

Materials Research, Geology, Archaeology, Forensic Applications, Ecology, Numismatics, Paint, and Paper/ Baun and Solomon [214] have used the effects of chemical combination on the X-ray emission spectra (line shifts, intensity changes,

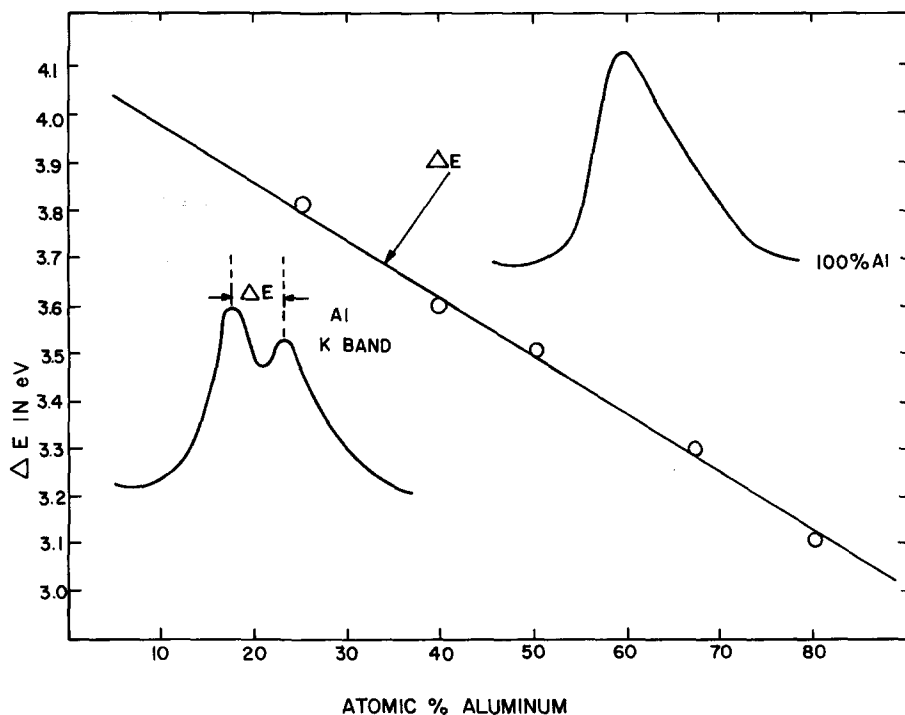


Fig. 34—The effect of composition in Al-Cu alloys on the Al $K\beta$ band features. The splitting in the Al $K\beta$ band ΔE , is plotted as a function of the atomic percent Al. Curve from Baun and Solomon [214].

line shapes, appearance and disappearance of lines) measured in the EPA to solve some problems difficult to approach in any other manner. Figure 34 illustrates the splitting of the Al K band ($K\beta$) that occurs in Al-Cu alloys and shows the systematic energy separation (ΔE) between the band features as a function of Al concentration. The quantitative potential of such a curve is obvious. Baun and Solomon used this curve to study the metallurgical transformation taking place when a Cu ball impacts upon an Al target in hypervelocity impact studies. The Al emission spectra from the bottom of the crater proved that actual alloying rather than intimate mixing had taken place. They also used the Fe L emission spectra to differentiate between FeO, Fe₃O₄, and Fe₂O₃ in oxidation studies on steel, a task which can be extremely difficult when measuring only Fe or oxygen intensities or both, particularly when the oxide scale is not well developed or condensed.

Hutchins [215] recently reviewed the application of the EPA to surface analyses, with emphasis on impurity segregation, specimen preparation and thin films. She effectively demonstrated problems encountered in specimen preparation, such as the preferential surface removal of Ti during the electropolishing of a Ta-20 Ti alloy. She also reviewed her earlier work [216], in which she derived a method for calculating the film thickness of Au films on Si using measured intensity ratios. Butz and Wagner [217] have measured a linear relationship on a log-log scale between the Mo $L\alpha_1$ X-ray intensity and the Mo layer thickness for Mo films on W substrates. Layers as thin as 2 Å were measured and the optimum sensitivity occurred when $E_0 = (3 \text{ to } 4)E_c$ (Mo $L\alpha_1$).

Kniseley, Laabs, and Fassel [218] have added a detection system to their EPA for detecting and measuring the intensity of the electron excited optical fluorescence (cathodoluminescence). Using this technique they obtained a detectability limit of 50 ppb Pr in La₂O₃. In other work Kniseley et al [144] reported detectability limits of 1 ppb Dy, Tb, and Pr in Y₂O₃, corresponding to mass sensitivities the order of 10^{-17} to 10^{-18} g.

O'Boyle et al [219] have used the EPA to correlate the composition of fission product inclusions generated in an UO₂-20 PuO₂ fuel element with the structural features that are representative of irradiated mixed oxide fuels. Their work demonstrates that meaningful research can be carried out when carefully obtained EPA results are combined with cognizant metallurgical interpretation. In addition to a high background noise level due to gamma activity, highly radioactive specimens pose problems in handling and prep-

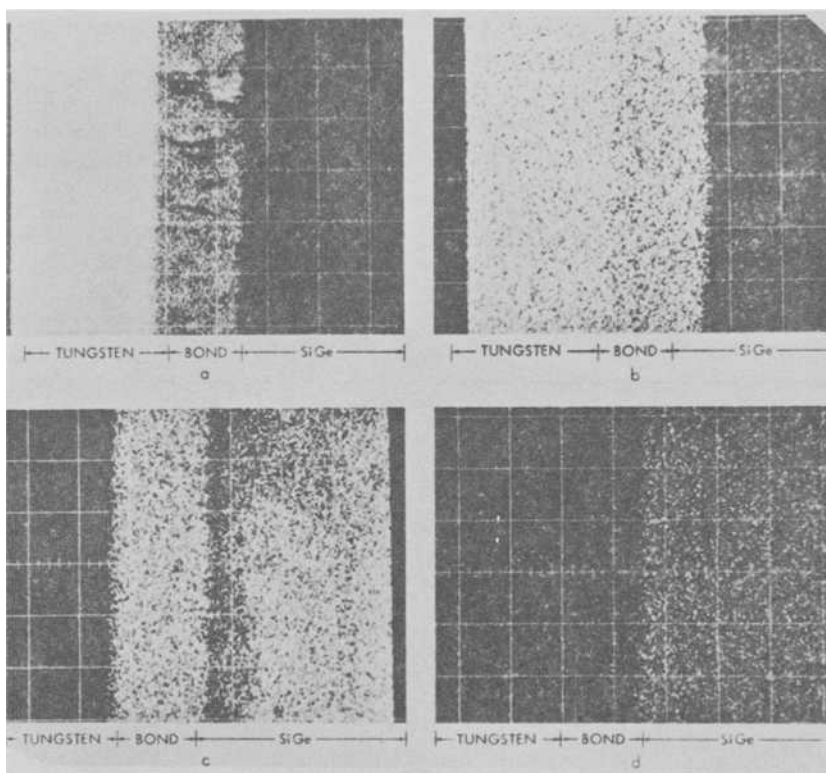
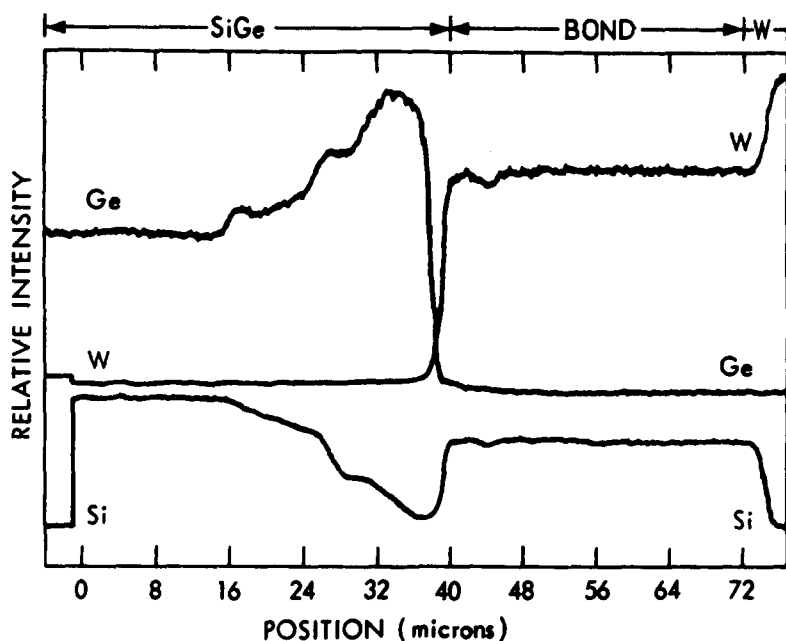


Fig. 35—The diffusion bonding of SiGe and W. On the graph (top) the Ge $K\alpha$, W $L\alpha$, and Si $K\alpha$ X-ray intensities are plotted as a function of position across the bond between SiGe and W. Regions of depletion and enrichment are clearly evident. The backscattered electron image and the X-ray scans for W, Si, and Ge are shown (bottom) in a, b, c, and d, respectively. Data and photos from Kobren [220].

aration. O'Boyle et al measured the variation of Ru, Mo, and Tc in inclusions in the columnar grain region of a fuel element and also the concentration of U and Pu in a mixed oxide matrix. Their data reveal the diffusion of Pu up the temperature gradient. They also found that the partitioning of solid fission products between

the matrix and inclusions could be accounted for theoretically.

Kobren [220] has written a fine NASA technical note describing the use of the EPA in several areas of materials research such as diffusion, alloy development, failure analysis, friction, and wear. Figure 35 shows the effects of diffusion bonding SiGe

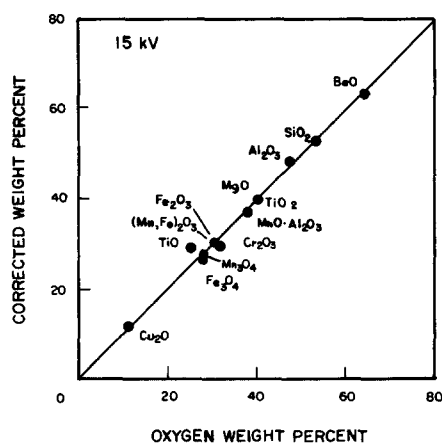


Fig. 36—The quantitative determination of the oxygen content of several oxides using the electron probe analyzer and a ZAF correction scheme. The corrected weight percentage calculated from the measured intensity ratio is plotted as a function of the oxygen content of the oxide. Data from Shiraiwa and Fujino [224].

to W and indicates extensive diffusion of Si in the formation of a W-Si compound in the zone of bonding.

Eichen, Kunz, and Tabock [221] have written a report describing the use of the EPA in automotive research. Landstrom and Kohler [222] performed a thorough examination into the applicability of the EPA to the study of particulate material, in particular, the study of automobile engine exhaust matter down to about $0.1\ \mu\text{m}$ in diameter. They established the feasibility of such studies, obtained meaningful results, and outlined important precautions in sample preparation and analysis. They found regions of high Pb content to be high in Cl and Br; the concentration of Pb, Cl, and Br increased as the particle size decreased. P, Zn, and Al were also associated with Pb; Ca, Fe, and Si were segregated, but not necessarily in Pb-rich areas. S was shown to exist primarily as CaSO_4 rather than as PbS in a comparison of the S emission spectrum from those two compounds with that of the exhaust sample. Semi-quantitative analyses were performed, yielding (in percent) 17.6 Pb, 2.7 Cl, 4.3 Br, 1.0 Al, 3.5 Zn, 0.2 Fe, 0.3 S, 0.5 P, 4.1 Si, 0.2 Ca, 11.5 C, plus unmeasured amounts of H, O, and N. The effectiveness of measuring elemental ratios (Ca/Si, Ca/Al, Si/Al) in particles of varying size and shape was indicated, as was the need for automation in the analysis of large numbers of exhaust particles.

Shiraiwa et al [223] discuss several areas of interest in the analysis of steel with the EPA. They present results of the quantitative analysis of 18 nonmetallic inclusions (carbides, nitrides, oxides, sulfides) in steel and correlate measured chemical concentrations with optical appearance. They

collected data for the B $K\alpha$ peak shift for AlB_{12} , BN, B_2O_3 , FeB, and $(\text{Cr}, \text{Fe})_2\text{B}$, in addition to the most efficient excitation voltage for several oxides, carbides, and borides.

Shiraiwa and Fujino [224] report some surprisingly good results for the quantitative determination of oxygen in several oxides (BeO , SiO_2 , Al_2O_3 , MnO , MgO , TiO_2 , Cu_2O , Mn_3O_4 , Fe_2O_3 , Fe_3O_4 , and $(\text{Mn}, \text{Fe})_2\text{O}_3$). They used a ZAF correction scheme [117, 225] and $(\mu/\rho)^{\text{OK}}$ values from various sources. Their results, obtained at 15 kV, are shown in Fig. 36 and indicate an average error of less than 5 percent.

Shaffer and Shebly [226] used the EPA in analytical numismatic applications, for example, to ascertain that a digit on a valuable coin had been soldered in place by detecting the presence of Pb and Sn. The nondestructive nature of the technique is particularly useful in numismatic and forensic applications. Ogilvie [227] used the EPA in 1960 to examine paint samples obtained with a hypodermic needle in the detection of art forgeries.

Butler [228] used the EPA in the forensic analysis of paint samples and has shown that a layer-by-layer analysis of multilayered, dried paint chips is possible. The techniques developed by Ficca [229] are also useful in paint analysis. Ficca developed a technique for analyzing the cross section of paper specimens, based primarily on the application of two to three coats of varnish to each side of the paper. He has been able to effectively show that most commercial papers are two sided with higher TiO_2 concentrations on the felt side. The Ti distributions in two commercial papers are shown in Fig. 37.

The EPA is particularly useful in segregation studies. Hutchins [215] detected concentrations of Fe at a 500-ppm level in a high purity Ta foil with an average Fe concentration of 8 ppm (emission spectroscopy). Melford [230] studied the segregation of Ni, Cu, and Sn in prior austenetic grain boundaries near the surface of mild and low alloy steels oxidized between 850 and 950 C.

The C contamination notable in electron beam instruments can be of use in the labeling of highly valuable items. A pattern such as, say, the owner's initials can be developed in the EPA by C contamination. It is possible to have this done automatically when programmed stage or beam position control is available. At any later date the C X-ray image can be used to identify the item.

Isasi [231] has used an oozing technique to identify the corrodants associated with intergranular stress corrosion cracking in austenitic steels. A low vapor pressure organic solvent, in which the suspected chemical species is soluble, is forced into

grain boundary cracks during polishing. The solvent oozes out in the microprobe forming a liquid film containing the corrodants (the dark band in Fig. 38a). In this particular case, the elements associated with the crack were Na, Cl, P, and O and their distributions are illustrated in Figs. 38b-d. Na, Cl and P were not detectable in the organic solvent.

Kyser and Wittry [232] have studied the dependency of infrared intensity on average carrier concentration in GaAs at 300 K in an EPA. Some of their results are shown in Fig. 39. The average infrared (IR) intensity values were obtained at 30 kV with a beam current of 100 nA by rapid scanning of the electron beam along a $250\text{-}\mu\text{m}$ -long line. In their work they found that for the low injection case, when non-radiative recombinations are predominant, the average intensity of the measured IR radiation increases with carrier concentration. Because of the large variation of IR intensity in specimens with about the same carrier concentration, they suggested that purity and crystal perfection may be most important in determining the radiative intensity.

Rao-Sahib and Wittry [233] have developed a method, based on the voltage dependence of cathodoluminescence, to

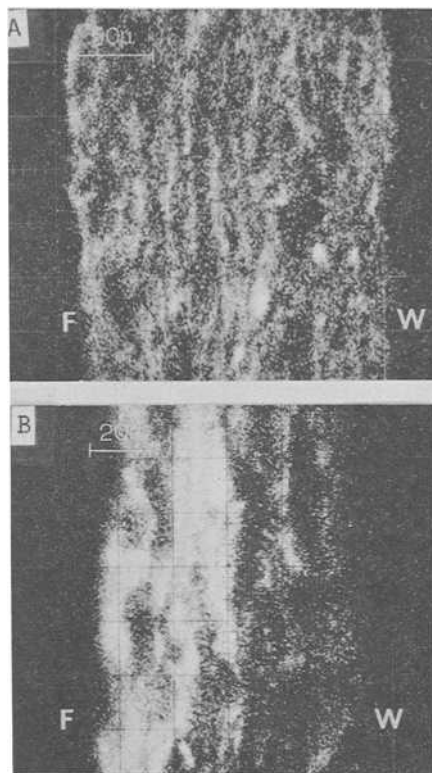


Fig. 37—The distribution of Ti in two commercial papers. A shows a fairly uniform distribution of TiO_2 from the felt side to the wire side of the paper, while part B illustrates high TiO_2 on the felt side. Photographs courtesy of Ficca [229].

measure the diffusion length in specimens (p-type GaAs) where the intensity of cathodoluminescence is not linearly related to the specimen current. Wittry [234] studied the effect of impurities on the intensity of cathodoluminescence in Te-doped GaAs.

The use of color to indicate different phases and elements in X-ray area scans has become increasingly popular, because color micrographs often simplify the interpretation of scanning data and because they can be easily, and in some cases inexpensively, produced. Three different approaches to the generation of color photographs representing the elemental distribution measured in the electron probe have been reported [235–238]. (1) The use of a three-gun color CRT, as described by Ficca [235], allows for the simultaneous imaging of any three outputs signals (X-rays, specimen current, backscattered electron current, secondary electron current, cathodoluminescence). (2) The conventional black-and-white images obtained using a single-gun CRT can be combined into a single color print by sequentially photographing them on color films with a photographic copier. In this method, recently described by Yakowitz, Heinrich, and Vieth [236], each sequential exposure is made with a different color filter placed between the camera lens and the positive black and white print. The method is inexpensive and rapid, and when care is taken to achieve registration of the different photographs excellent results are obtained. (3) It is also possible [237] to insert color filters between the single-gun CRT screen and the camera on the electron probe. The various signals are again sequentially recorded using a different filter for each signal.

Yakowitz [238] has written a definitive review on the uses of various color techniques in metallography. The use of color composites in electron beam scanning considerably simplifies the correlation of compositional information heretofore presented on separate X-ray area scans and current images.

The effectiveness and aesthetic value of the technique should become apparent in the discussion of geological and archaeological applications to follow. Figure 3 is a color composite photograph of a portion of a glass spherule found in lunar soil. Adler et al [239] studied the metallic inclusions in these spherules and found them to contain primarily Fe and Ni. The presence of these micrometeorites was considered to indicate that the glassy bodies were formed by impact melting rather than by a volcanic process. In Fig. 4a [240] a color composite illustrates the phases found in a basaltic rock from Apollo 11. In Fig. 4b metallic iron and troilite inclu-

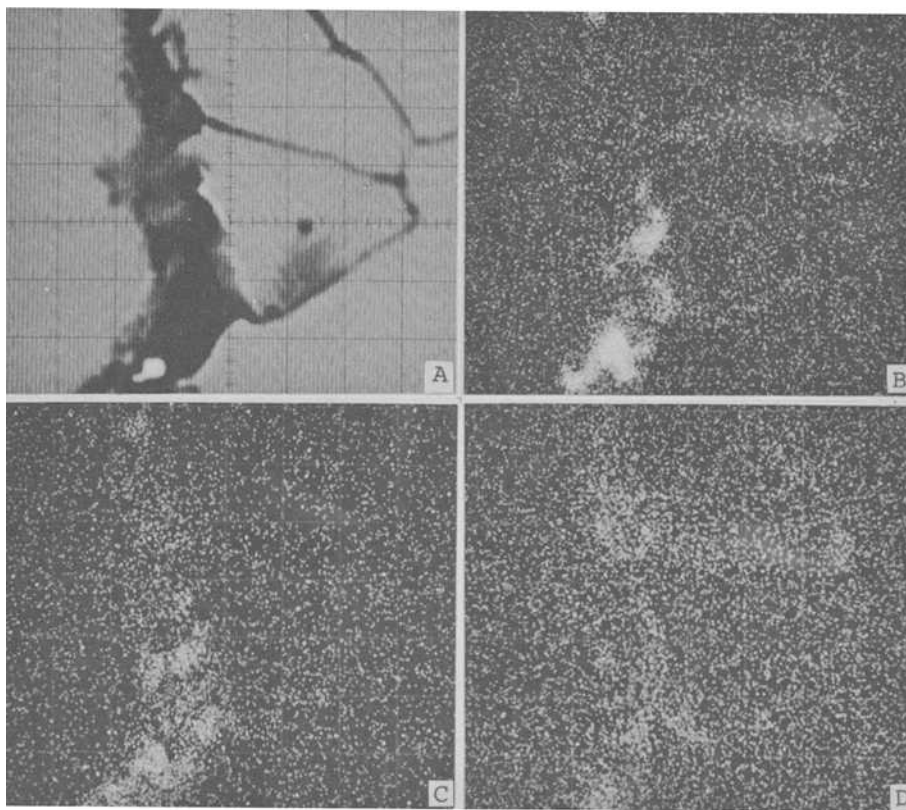


Fig. 38—Determination of the corrosion products associated with intergranular stress corrosion cracking in an austenitic steel by the use of an oozing technique. (a) Specimen current image, (b) P X-ray image, (c) Na X-ray image, and (d) Cl X-ray image. The wide, dark region running from the top to the bottom of the specimen current image indicates the liquid film which has oozed out of the grain boundary. Magnification: 800.

sions, which are absent in terrestrial basaltic rock, are indicated in a basaltic rock sample from Apollo 11. Figure 5 shows a terrestrial basalt [240]. French, Walter, and Heinrich [241] have determined the quantitative mineralogy of a lunar rock sample with an EPA.

Ficca [235] has demonstrated the advancement in technology which occurred in the manufacture of bronze with the help of an EPA to examine archaeological artifacts from southern Sumaria (1965–1966 survey) and identified different inclusions in older (3500 B.C.) and newer (400 B.C.) samples. Figure 6 illustrates the use of the three-gun color CRT technique and indicates the high Cu content of an inclusion in the 400 B.C. sample.

Biological Research, A Promising Area/ One of the most intriguing areas of EPA application is that of biological research, an area where exciting achievements should be anticipated.

Problems with Biological Materials—The reason that the biologist has not enjoyed the success that the metallurgist or geologist has in his use of the EPA is a series of difficult problems arising from the unique nature of his specimens in an EPA environment. The biological specimens

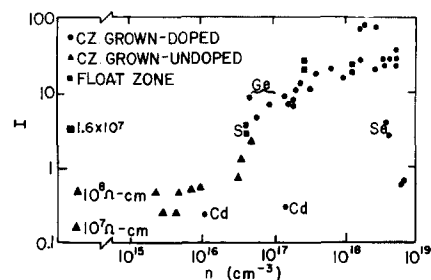


Fig. 39—Average infrared (IR) intensity I versus average carrier concentration n for GaAs at 300 K. Unless otherwise noted in the graph, all specimens with $n < 10^{16}/\text{cm}^3$ were Te doped and those with $n > 10^{16}/\text{cm}^3$ were undoped. CZ grown means Czochralski grown [232].

receiving the greatest attention are soft tissues and blood containing 50 to 90 percent H_2O , teeth and bone in various stages of mineralization, and plants. Teeth and bone are easily prepared and can be studied in the EPA using conventional specimen preparation and analysis techniques. Soft tissues, plants, and blood, on the other hand, pose many problems. Because of their low density ($\sim 0.4 \text{ g/cm}^3$), the penetration and spread of electrons in such bulk materials is large when normal accel-

ation potentials (15 to 30 kV) are utilized.

Andersen [242, 243] has demonstrated the feasibility of studying bulk soft tissue at low voltages using longer wavelength X-ray lines in order to retain an over-voltage for satisfactory X-ray generation while maintaining a 1- μ m resolution capability. Hall [244] describes the use of thin films to restrict electron diffusion and high voltages to provide sufficient X-ray generation in the thin film. The thin film has the advantage that its microscopic appearance is familiar to the biologist, particularly if it is stained and on a glass slide. The following comprise a list of some of the identified problem areas in biological applications.

1. Specimen preparation—It is usually essential that the specimen be unaffected in any manner by the preparation procedure. This means that the structure and elemental distribution must remain unaltered. To prevent the addition, removal, or migration of elements, freeze drying and cutting of tissue specimens is often employed rather than conventional fixing, embedding, and staining processes. The latter, however, provide optimum histological correlation and the thinnest possible films.

2. Homogeneity—Biological structure is often complex, with chemical heterogeneities occurring on the micrometer level. This is particularly troublesome from an electron penetration point of view, as it is possible even at low voltages to penetrate the examined constituent to another one beneath it, particularly in bulk specimens. Chemical heterogeneity on the micrometer level in biological specimens can cause large X-ray signal variations without an increase in the concentration of the element of interest.

3. Resolution—To achieve a 1 μ m spatial resolution will, generally, require thin films. In some cases, low voltage operation with well characterized bulk materials will provide the needed resolution.

4. Density—Biological structures can vary in density without significant changes in composition. Hall [244] has done some good work in this area and developed theoretical and experimental methods for distinguishing chemical changes from density variations in thin biological specimens. Continual monitoring of C, O, or N radiation can also be helpful in such cases. Thickness variations, encountered during the preparation of 0.1 to 3 μ m films of uniform thickness, can pose similar problems.

5. Overlay—Experimental verification is needed in some cases to ascertain whether or not the examined constituent is covered or surrounded by another constituent, for example, in dried blood smears plasma may overlay or accumulate or do both at the

edges of the cellular constituents.

6. Water—The high water content (50 to 90 percent), which is mostly removed during specimen preparation and to a much lesser extent in the EPA vacuum, can lead to the redistribution, loss, or both of diffusible ions. The use of an environmental stage of the type described by Lane [245] would permit the examination of undried tissue.

7. Elemental sensitivity—The present sensitivity of an EPA for the biological building blocks (C, O, and N) is not good; however, the sensitivity for most other biologically important elements (Na, Mg, P, S, Cl, K, Ca, Fe, Cu, Zn, and I) is satisfactory.

8. Normal variability—The concentrations of many elements in normal biological materials can vary considerably, making exhaustive analysis of normal materials an absolute prerequisite for the study of abnormal materials. This is certainly an unfamiliar situation to the materials scientist, who often finds the normal and abnormal situations in the same specimen.

9. Thermal sensitivity—Because of their low thermal conductivity, soft tissue and blood specimens can be easily damaged from the heat generated by the electron beam. This heat sensitivity can manifest itself through the redistribution or loss of elements, the removal of water, the generation and subsequent loss of volatile compounds, or the incineration, with the subsequent deposition and perhaps concentration, of certain elements.

10. Electrical conductivity—Most specimens need to be coated with a thin (100 to 500 Å) conductive coating of C, Ag, Al, Ni, or Au to prevent charging. Such coatings may (a) absorb X-radiation of interest, (b) reduce the energy of the incident electrons, (c) generate fluorescent radiation in the specimen, (d) adversely affect the optical appearance of the specimen, (e) prevent the accurate analysis of the element used as the coating, for example, C; and (f) become unstable and introduce counting fluctuations.

11. Analysis time—Each problem may require a different preparation and analysis procedure, leading to long times per analysis or investigation. Our own experience is that one order of magnitude more time is required to fulfill a service request in the biological area as compared to the metallurgical area.

12. Concentrations—The elemental concentrations of interest are very often near the EPA detectability limits of 50 to 1000 ppm. One would certainly expect the IMA to be of use in biology because its detection capability lies in the ppb to ppm range.

13. Biological variation can occur with-

out chemical or structural variation, for example, different degrees of mineralization can have the same Ca/P ratio. While the above problems can be troublesome, we believe that in most cases they can be solved. The following problems present more serious obstacles.

14. Quantitation—Successful quantitation has been achieved only in a few investigations. The accuracy of any quantitative method using biological standards, a ZAF scheme, or Hall's thin film model has not yet been established. The technique of Hall [244], in which the ratio of the characteristic X-radiation to continuous X-radiation is monitored, appears to offer the most promising method for measuring absolute concentrations in thin films. Fortunately, standards with a known composition similar to the unknown are often available. Much information can be extracted by comparing normal and abnormal specimens, provided the artifacts of density and thickness variation are accounted for.

15. Contamination—This is always a serious problem in biological research, particularly when the element of interest is present at levels near the detectability limit. Specimens can be contaminated during collection, preparation, transfer to the EPA, and analysis (C deposition). The effect of contamination can be extremely difficult to identify and can lead to serious errors in interpretation [206]. The source animal or plant could also have been contaminated by its environment or treatment prior to specimen collection.

16. Biomedical significance—Any measured localized chemical variations must have biomedical significance and should not be made known unless they make some sort of biological sense. If biomedical significance is lacking, the findings must be presumed to be due to contamination or artifacts. It is this problem that makes a good working relationship between the biologist and X-ray analyst a most rewarding and productive one.

17. Correlation of chemistry and morphology—The image contrast available in conventional EPAs when examining biological materials with small Z variation is, at best, inadequate. X-ray and specimen and backscatter current images in many cases are nearly worthless. In our own laboratory, several approaches to the problem are being pursued. (a) Improved specimen current amplifiers, such as the one described by Heinrich et al [246], could provide improvements in the specimen current image. (b) The addition of a high quality, secondary electron detection system would provide good SEM images; however, in the flat, thin films needed for quantitative analysis the contrast available may be insufficient for the needed correla-

tion of structure and chemistry. (c) A metallic substrate such as Si offers the advantages of high purity, good conductivity, which eliminates the need for coating, and high reflectivity. Thin films on such substrates can be examined in a reflected light microscope, much to the chagrin of the biologist used to observing stained sections in transmitted light. By careful and painstaking examination of unstained thin films of known cellular structure on Si (sometimes followed by staining), it is possible to learn to identify certain constituents. (d) Stains can be helpful, but a detailed investigation is then needed to determine the effect of the stain on the elemental distribution and concentration. (e) A TEM attachment certainly provides the most satisfactory image, but the specimens must then be subjected to the rigors of fixing, embedding, cutting, etc., in order to obtain a 500 to 1000-Å film for use in an EPA with a maximum high voltage capability of 50 kV. (f) High purity quartz substrates (99.9999 percent SiO_2) can be used in transmitted light, but the contrast is generally poor particularly after the required conductive coating has been applied. (g) Microincineration techniques are of considerable interest in specialized areas and they are sometimes possible to carry out with the electron beam of the probe. A careful study of the structure before and after incineration is essential. (h) Serial sections, one on glass and the next on the selected substrate, are sometimes useful.

These problems indicate why success in the biological area has been so much more elusive than in materials science and mineralogy. Nevertheless, all of these problems can be overcome in most cases, and the potential contribution is so great that the effort expended to overcome the difficulties will certainly be justified by the results of the research. The following list of areas of application and useful techniques hopefully will eliminate the dismal picture conjured up by the preceding list of problems.

Areas of Possible Usefulness—Successful research efforts have been realized or are expected in such areas as (1) mineralization of bone and teeth; (2) the effectiveness and reliability of histochemical stains; (3) the study of body fluid residues, for which less than a nanoliter of fluid is required; (4) the effect of implant materials on surrounding tissue and body chemistry; (5) the localized chemical analysis of normal and abnormal cellular constituents; (6) the analysis of biological particulate matter—Heinz bodies, Jolly bodies, etc.; (7) the identification of foreign particulate matter—asbestos particles, paint pigments, coal dust, etc.—and the effect of such material on surrounding tissue; (8) toxicology; (9) plant and human pathology; (10) evaluation of

microincineration techniques using heat, electron beams, plasmas, etc.; and (11) virus studies.

Successful Applications—Still, some fine work in the biological area has been completed, as evidenced by the following recent applications in biological research. Schafer and Chandler [247] analyzed the centrioles in the distal renal tubule of a normal guinea pig using the EMMA 4. These centrioles, which could not be isolated from other cellular constituents, measured 0.2 by 0.5 μm and contained expected levels of K and Cl but unexpected levels of Si and S. Their 700-Å tissue section (required for TEM) underwent a complete fixation, embedding, etc., preparation procedure.

Rasmussen, Shull, and Dryer [248] and Rasmussen [249] studied the penetration and subsequent effect of AlCl_3 on the growth of corn. The study was prompted by the need to understand the pathology of tobacco grown in acid-containing soil. By studying the distribution of Al, Ca, P, and K in 16- μm -thick sections with an EPA they were able to determine the mode of entry and distribution of Al in the plant. When lateral roots were present, Al was only found in the cortical tissue; otherwise, it was concentrated at the root surface, the epidermal cells serving as an apparent barrier. Rasmussen proposed that, when the secondary or lateral root breaks through the epidermis of the parent root, a path becomes available for the Al to enter both the main and secondary roots prior to the formation of the endodermis. Figure 40 [249] illustrates the simultaneous presence of Al and P in the cortical tissue of a lateral root. The Al precipitates as a phosphate, causing a phosphate deficiency which is secondary to the direct effect of Al. Waisel et al [250] have also pursued this problem but do not agree with the results of Rasmussen [249]. Humble and Raschke [251] have recently found, using the EPA in the EBS mode, that the guard cells around the stomate are high in K when the stomate is open and low in K when the stomate is closed. Kaufman et al [252] have reported Si concentrations in the guard and subsidiary cells of the stomatal apparatus.

Carroll et al [253] have used the EPA to localize Pb, Ca, and P in the kidney tubules of Sprague Dawley rats fed with a 1 percent lead acetate solution. Figure 41 contains EBS photographs illustrating these concentrations in 20- μm -thick paraffin embedded tissue sections. Carroll et al believe this work proves that Pb is deposited in the kidney and lends support to the theory that Pb poisoning is associated with the creation of lead protein complexes. Robison and Davis [254] have found that the I concentrations and dis-

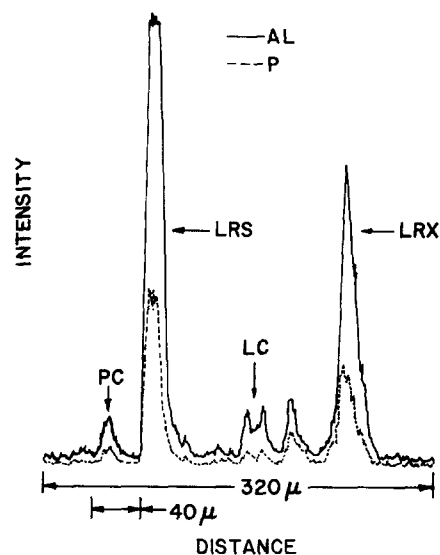


Fig. 40—Al and P X-ray intensities plotted (top) as a function of location in a traverse across a longitudinal section of a lateral root. PC = parent root cortical tissue; LC = lateral root cortical tissue; LRS = lateral root surface; LRX = lateral root xylem. Data from Rasmussen [249]. A secondary electron image (bottom) of a corn root showing the ruptured surface due to the emerging secondary (lateral) root is shown at a magnification of 300.

tributions in rat thyroid follicles are the same whether the animal is on a low or high I diet. Galle et al [255] used an EPA-TEM combination instrument to measure the Au concentration in the kidneys of rats. They were able to describe the process of Au poisoning by the Au salt aurothiopropanol. Galle et al [256] have used the IMA to study renal tissue and red blood cells (RBC) and estimated that 10^{-20} g of Na would give a satisfactory image of a RBC in 0.03 s. There are about 3×10^{-16} g of Na per cubic micrometer of RBC.

We have looked for the Pt from the Cis-Pt(II) compounds given to mice with Sarcoma 180 tumors by Rosenberg and VanCamp [257]. There is a remarkable regression of the tumor after such treatment and, hence, a need for understanding the role of Pt. Pt was not detected with

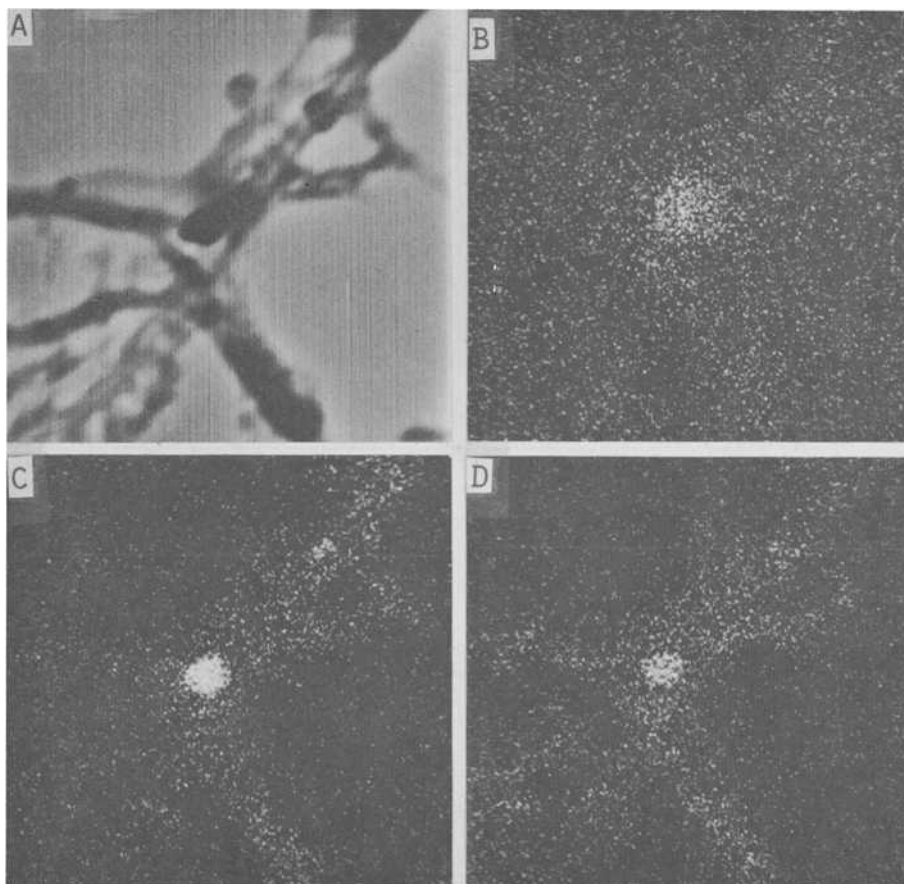


Fig. 41—The distribution of Pb, Ca, and P in the kidney tissue of rats after Pb poisoning. Specimen current, Pb X-ray, Ca X-ray, and P X-ray images are shown in A, B, C, and D respectively. The scans covered a 100 by 100- μm area and the analysis was performed at 35 kV using a specimen current of 100 nA. Photographs courtesy of Carroll [253].

the EPA in five frozen sections of liver spleen or tumor from treated mice; however, Shull [251] did locate significant levels of Pt in the circulating blood using the EPA.

Rabideau and Florin [258] studied the residues of anomalous water prepared in quartz capillaries. They used an EPA because of the great difficulty involved in producing sufficient quantities of polywater for analysis by conventional techniques. The principal constituents of the residue were Na, B, and O with smaller amounts of Cl and Si; N, S, P, K, and Ti were not detected. Na, Si, and Cl X-ray scans of the residue are shown in Fig. 42. Using solutions of known concentrations they estimated levels of 4 percent B and 6 percent Na and concluded that, since apparently significant amounts of inorganic salts are present in polywater, there is good reason not to accept the hypothesis that polywater is a true polymer of water.

Using reference solutions, Morel and Roinel [259, 260] have developed methods for quantitatively analyzing residues from liquid samples of less than 10^{-9} liter in volume. Hogben and Ingram [261] have

worked for several years developing unique techniques for studying biological fluids.

Gardner and Hall [262] used an EPA to examine the extent to which a Ag stain (v.Kossa technique) indicates the concentration of Ca and P in the mineralized and unmineralized epiphyseal cartilage of young turkey bone. They found that Ag was deposited only at localized high Ca concentrations (well mineralized) and concluded that the v.Kossa method does provide an extremely precise indication of the site of insoluble Ca salts in calcified sections of mineralized avian cartilage. Hale [263] employed the Gomori technique (precipitation of black cobalt sulfide) for locating an enzyme (alkaline phosphatase) and found Ca, P, S, and Co at the same sites in rat kidney. In another bone study Johnson [264] studied the Sr content in rat femurs and found an increasing Sr/Ca ratio in the diphyseal bone from the midlength toward the extremities.

Several good studies on the distributions of elements in teeth [265–269] have been published. The two areas of greatest interest are the prevention and reduction of dental caries and the characteristics and

effectiveness of dental amalgams. We have studied the effectiveness of a compound painted on teeth in generating an F gradient in the enamel; the results are shown in Fig. 43. The average F concentration measured with a 100 by 4- μm line in an EPA decreases sharply as one moves into the enamel and falls below the detectable limit of 400 ppm F at about 14 μm from the edge. On the other hand, when a 4- μm spot is used an extremely nonuniform distribution of F was observed, ranging from about 2000 to 5000 ppm F at 2 μm from the edge. F exceeded the detectable limit (650 ppm) as deep as 30 μm into the enamel. Saffir et al [270] studied the F concentrations in teeth and reported detectability limits of 50 ppm. The work by Saffir [265] represents an exhaustive study of the dietary effects on teeth.

Banfield et al [271] studied asbestos particles less than 1 μm in diameter by 40 to 60 μm long and anthracotic pigment (coal dust) in human lung tissue and reported the presence of Ti. Thomas and Corlett [272] examined TIV (tipula iridescent virus) in an EPA before and after plasma ashing [273]. By observing the P distribution and then studying the ash in an electron microscope they determined the location of the DNA within the virus.

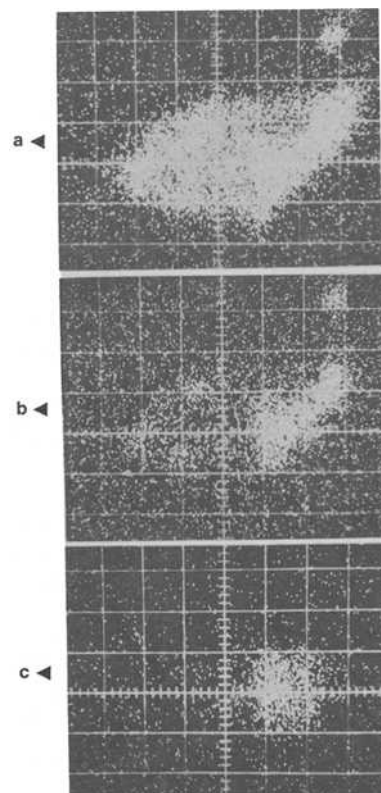


Fig. 42—X-ray images of anomalous water residue. The three scans at a magnification of 2000 for (a) Na, (b) Cl, and (c) Si were obtained with an ARL EPA. Photographs courtesy of Rabideau and Florin [258].

We have mentioned a few of the most recently published reports. Hall [274] has available a complete bibliography covering the period from 1959 to March 1969. It is interesting to note that of about 90 references Hall is one of the authors 23 times, Calle 12 times, Höhling 11 times, and Tousimis 10 times, which may serve to point out those laboratories at which heavy emphasis is placed on biological research with the EPA. Solutions to some of the problems discussed previously would do much to promote increased activity in biological microanalysis, from which meaningful research results and important humanitarian contributions in biology are certain to result.

The next section is included as a guide for the effective pursuit of additional knowledge in the field of electron beam microanalysis.

Suggestions for the Novice

Books and Review Articles—A Planned Reading Program/ To the newcomer we suggest the following program as a rapid and effective introduction to scanning microanalysis. A few days of straightforward reading is the first and most important step. Chapters 1, 2, 4, and 10 in *X-Ray Absorption and Emission in Analytical Chemistry* by Liebhafsky et al [275] should be followed by the complete "The Electron Microanalyzer and Its Applications." The latter is unpublished and is only distributed to participants in a two-week summer course offered at MIT under the direction of R. E. Ogilvie [276]. Copies can be borrowed from past participants. Chapters 8 to 12 in *Electron Microscopy and Microanalysis of Metals* [277] provide an introduction to applications in metallurgy. At this point, while it may seem rather mundane, we suggest perusing the literature provided by the various equipment manufacturers. EPA, SEM, and IMA manufacturers are listed in Table 18.

Probing more deeply now, the review by Philibert [11] entitled "Electron Probe Microanalysis" is an excellent article and represents a thorough updating of the earlier review by Castaing [12]. The review by Poole and Martin [51] is outstanding in its coverage of instrumental and experimental aspects and lists 299 references, which will thoroughly acquaint the beginner with the literature. The recent review by Martin and Poole [278] is a good presentation of the state of the art of quantitative analysis through 1969. The short but remarkable paper by Wittry [279] represents a major contribution to the understanding of microanalysis notwithstanding its early publication date. A lucid picture of the physics of quantitative analysis is presented in a paper by

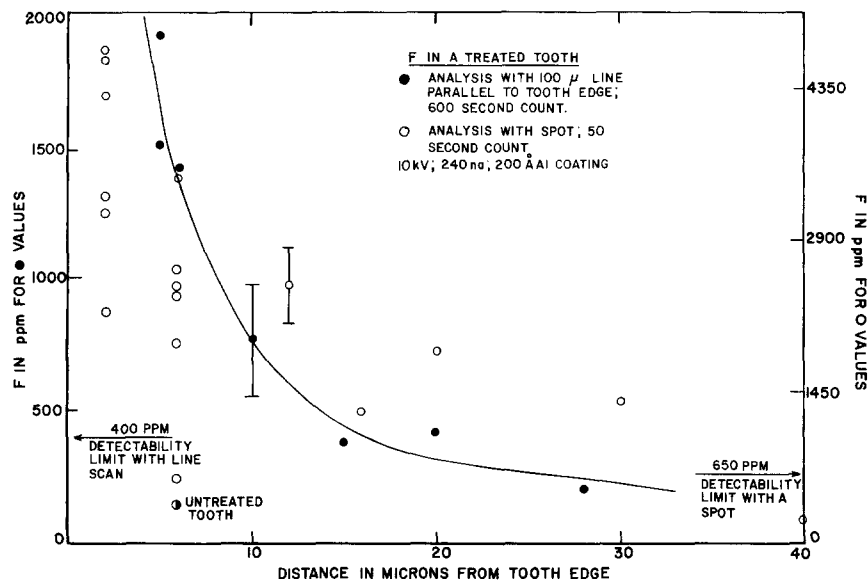


Fig. 43—The penetration of F into tooth enamel. The F concentration in ppm is plotted as a function of the distance from the tooth surface. The curve drawn through the darkened circles represents the analysis for a 100- μ m-long line and measures the average F concentration. The right-hand concentration axis corresponds to the open circles, which represent several point analyses and show considerable heterogeneity. The precision in the case of the line analyses was ± 200 ppm and the point analyses ± 360 ppm.

Duncumb and Shields [280]. Philibert has published two thorough discussions [281, 282] of quantitative analysis. If your particular interest is in biological applications, the papers by Andersen [283] and Hall [244] are suggested; mineralogical applications are covered in the papers by Sweatman and Long [284], Kiel [285], and Long [147]; electronic devices and cathodoluminescence are discussed by Kyser and Wittry [233]; metallurgical applications are reviewed by Goldstein [286]. These papers are of a general nature and, therefore, are good reading regardless of your particular interest. Reading and assimilating this material can be accomplished in one to two months, particularly if one is willing to sever his telephone wire.

National and Local Meetings/ At this point a membership in EPASA—Electron Probe Analysis Society of America—would be most valuable and can be obtained by requesting a membership application from the secretary of the society [287]. Attendance at the meetings of one of the local probe users groups (Table 19) can be an extremely valuable, stimulating, and interesting experience for a newcomer. These meetings are informal but informative and a free exchange of ideas is promoted. Specimens for analysis are distributed and group results are presented and discussed. Instrumental difficulties and performance are always rigorously discussed. Invited speakers on related topics are often present.

In the last three meetings of the Midwest Electron Probe Users Group the following subjects were discussed by invited

speakers or group members: quantitative analysis using EPAs and SEMs, the nature and performance of Li drifted Si detectors, automated EPAs, high resolution SEMs, crystal spectrometer attachments for SEMs, quantitative analysis of B_4C , ZrC, NbC, and TaC, X-ray crystal optics, the construction and use of an ultra microtome, the ion microprobe analyzer, the imaging mass analyzer, background corrections, the quantitative analysis of Fe-Ni-C alloys, and the analysis of microinhomogeneities in glass.

From Novice to Expert/ Somewhere along the line the analyst will encounter the need to review some statistics and there is no end to the number of available publications. References 288 to 291 are simple but thorough. As the investigator broadens his scope, NBS Special Publication 298 [292], edited by K. F. J. Heinrich—one of the finest EPA publications ever to appear—should be carefully studied cover to cover. It is a lucid state-of-the-art description of quantitative electron probe microanalysis.

As the novice becomes more expert, the publications covering the international meetings held at Tübingen [293], Orsay [294], and Stanford [295] offer excellent reference sources. The proceedings of the EPASA national meetings for the second through fifth [296–299] conferences contain extended abstracts that will give the reader a good idea of what has been done in the United States. *The Electron Microprobe* [300] is a complete compilation of the papers covering what has been referred to as the Zeroth National Meeting and

Table 18—Commercial Sources of EPAs, IMAs and SEMs

<u>Manufacturer and Equipment Available</u>	<u>Manufacturers or Representatives Address in USA</u>	<u>Abbreviated Name</u>
Advance Metals Research, Corp. SEM, TEM ¹	Same 179 Middlesex Turnpike Burlington, Mass.	AMR
Applied Research Laboratories, Inc. EPA, SEM, IMA	Same 9545 Wentworth Street Sunland, California 91040	ARL
Cambridge Scientific Instruments, Ltd. EPA, SEM	Kent-Cambridge Scientific, Inc. 8020 Austin Ave. Morton Grove, Illinois 60053	CAMBRIDGE
Goates and Welter Instrument Corp. SEM, TEM	Same 777 Pastoria Ave. Sunnyvale, California 94086	CWIC
Compagnie d'Applications Mechaniques a l'Electronique Au Cinema et a l'Atomistique EPA, SEM, TEM ² , IMA	Cameca Instruments, Inc. 101 Executive Blvd. Elmsford, N. Y. 10523	CAMECA
Etec Corp. SEM, TEM	Same 3392 Investment Blvd. Hayward, California 94545	ETEC
GCA Technology Div. IMA	Same Burlington Road Bedford, Mass. 01730	GCA
GEC-AEI (Electronics) Ltd. EPA ³ , IMA	AEI Scientific Apparatus, Inc. 500 Executive Blvd. Elmsford, N. Y. 10523	AEI
Hitachi, Ltd. SEM, TEM	Perkin-Elmer, Inc.-Ultek Division Box 10920 Palo Alto, California 94303	HITACHI
Japan Electron Optics Laboratory Co. EPA, SEM, TEM	JEOL, (U.S.A.) Inc. 477 Riverside Ave. Medford, Mass. 02155	JEOL
Material Analysis Company EPA, SEM, TEM	Same 1060 East Meadow Circle Palo Alto, California 94303	MAC
Packard Instrument Co. EPA	Same 2200 Warrenville Road Downers Grove, Illinois 60515	PACKARD
Philips Electronic Instruments, Inc. EPA	Same - Norelco Division 750 S. Fulton Ave. Mount Vernon, N. Y. 10550	NORELCO
Ultrascan, Inc. SEM, TEM	Same 18530 South Miles Parkway Cleveland, Ohio 44128	ULTRASCAN

(1) Where TEM is designated manufacturers supply a scanning TEM accessory to their SEM.

(2) This manufacturer provides a transmission electron microscope attachment for their EPA.

(3) A combined electron microscope-microprobe analyzer.

contains the commonly used mass absorption coefficients proposed by Heinrich and the most up-to-date bibliography (1966) on the EPA compiled by him. An updated version of the bibliography is presently being prepared by Heinrich. The First National Conference is partially covered in the book edited by Tousimis and Marton [301]. The proceedings [302] of a meeting sponsored by the National Science Foundation and the Japan Society for the Promotion of Science at the University of Hawaii in November 1968 represent a brief summary of the status of electron probe

analysis as of that date. A myriad of fine papers has not been mentioned as initial reading material, because they are more specific and the expert will be directed to them in his continued reading. The detailed review paper published in even years by *Analytical Chemistry* [303-305] is a good literature source and essential reading for all those active in the field.

The two-week summer course at MIT (see Table 19) on EPA and associated topics is recommended. A student will extract the maximum from this course if he has had some modest experience, or at

least a thorough introduction to the literature. Both lecture and laboratory sessions are held. The course is held every other year and will be offered next during the summer of 1972. A one-week course on both EPA and SEM will be offered this summer for the first time at Lehigh University. A three-day course on SEM was held in Boston in 1971 and will be presented again in 1972.

From this point on the paper will deal with the accumulation of precise experimental data and their conversion to accurate chemical compositions.

Table 19—Electron Probe Societies and Schools

<u>Name of institution</u>	<u>Location</u>	<u>For information contact</u>
Electron Probe Analysis of America-EPASA	U. S. A.	J. Brown, Faculty of Engineering Science, University of Western Ontario, London, Ontario, Canada
<u>Local Probe User Groups*</u>		
<u>Domestic</u>		
Bioprobe	A newsletter circulated to persons with interest in biological applications	J. R. Coleman, Dept. of Radiation Biology and Biophysics, Un. of Rochester, School of Medicine and Dentistry, Rochester, N. Y. 14620
Metropolitan*	Metropolitan New York City area	I. Payne, Bell Telephone Labs, Murray Hill, New Jersey 07974
Midwest*	Midwestern U. S.: Ill., Ind., Iowa, Mich., Minn., Mo., Ohio, Wisc.	V. Shull, Horticulture Dept., Mich. State Univ., Lansing, Mich. 48823
Northern California*	Northern Calif., Oregon, Washington	R. J. Ruscica, Materials Analysis Co. 1060 East Meadow Circle, Palo Alto, California 94303
Pittsburgh*	Pittsburgh Metropolitan area, Ohio, Pa.	J. Ryan, Harbison-Walker, R&D Center, Pittsburgh, Pa.
Southwestern*	Texas, Arizona, New Mexico, Louisiana, Oklahoma	W. Chambers, Sandia Laboratories, Box 5800, Albuquerque, N. Mex., 87115
Washington*	Washington D.C. Metropolitan area	J. Gilfrich, Naval Research Lab., Washington D. C.
<u>Foreign</u>		
Birmingham Probe Analyzer User Group	Birmingham, England area	A. Belk, Dept. of Metallurgy, Univ. of Aston in Birmingham, Birmingham 4, England
Canadian Probe Users Group*	Canada	R. H. Packwood, Dept. of Energy, Mines, and Resources, 568 Booth St., Ottawa, Ontario, Canada
French Probe Users	France	Mlle F. Maurice, A.N.R.T., Microprobe Subcommission, 44 Rue Copernic, Paris
Scandinavian Association of Microprobe Users	Scandinavian countries	L. Backerud, AB Sevenska Metallverken Finspong, Sweden
<u>Schools</u>		
Electron Probe Microanalysis and Scanning Electron Microscopy - Lehigh University	Bethlehem, Pa.	J. I. Goldstein, Dept. of Metallurgy and Materials Science, Lehigh Univ. Bethlehem, Pa. 18015
Massachusetts Institute of Technology Summer Course on Electron Probe Analysis	Cambridge, Massachusetts	R. E. Ogilvie, MIT, Room 13-4009 77 Massachusetts Avenue, Cambridge, Massachusetts 02139
Three Day Seminar in Scanning Electron Microscopy - Industrial Forum Associates	Burlington, Massachusetts	S. Moll, Advance Metals Research, Corp 179 Middlesex Turnpike Burlington, Massachusetts
Scanning Electron Microscopy, Intensive Short Course - State University College (State University of New York)	New Paltz, New York	A. V. Patsis, Professor of Chemistry State University College New Paltz, New York 12561

*Affiliated with EPASA

Part II—Experimental Considerations and Qualitative Analysis

Electron Beam

The Measurement of Accurate X-ray Intensity Ratios

What is required to produce an accurate and precise measurement with an electron probe is an astute analyst with a knowledge of the many artefacts and possible sources of error normally encountered. It is worth noting that electron probes must be directed and not administered. In the early days of microprobe analysis, when accuracies to within 5 to 10 percent of the amount present were common, there was no real need to concern oneself with many sources of error; but today, when accuracies to within 1 percent are commonplace, such effort is imperative.

The production of small errors (0.5 to 1 percent) has become a real source of inaccuracy. Several papers have discussed experimental error and eight in particular are of considerable value. Wittry's [279] report of nine years ago is a remarkable document and it is unfortunate that more investigators have not taken heed of the warnings presented therein. Poole and Martin [51] present a thorough discussion of experimental errors. Sweatman and Long [284] and Keil [285] discuss the problems encountered in geology. Hall [244, 306] and Andersen [283] do the same for the biological sciences. Heinrich's [116] paper summarizes some common sources of error. These are recommended reading on a periodic basis.

Theoretical Precision/ The goal in quantitative experimental measurement is to obtain as precise and accurate a value of k , the X-ray intensity ratio, as possible. In most cases k is the ratio of the intensity from an unknown to that from a pure or compound standard. Because X-ray emission obeys Poisson statistics [307] the variance σ^2 is given by the mean intensity $\bar{N}$; σ , the standard deviation, is $\bar{N}^{1/2}$; $\sigma/\bar{N}$, the fractional standard deviation, is $\bar{N}^{-1/2}$;

$$\sigma(x \pm y) = [(\sigma_x)^2 + (\sigma_y)^2]^{1/2};$$

and

$$\frac{\sigma(x/y)}{x/y} = \left[\left(\frac{\sigma_x}{\bar{x}} \right)^2 + \left(\frac{\sigma_y}{\bar{y}} \right)^2 \right]^{1/2}$$

The measured peak and background counts are P and B ,

respectively, and the superscripts prime and zero refer to the unknown and standard, respectively. Thus,

$$k = \frac{P' - B'}{P^0 - B^0}$$

and σ_k/k is given by Eq 7.

Ziebold [126] has derived the above expression for σ_k/k , which is a useful guide in evaluating instrumental and operator performance. In our own laboratories several standards of known composition are periodically analyzed to ensure continued optimum performance. If several measurements of P and B are made, σ_k/k represents the best possible precision when mean values of P and B are used. This value (Eq 7), based on counting statistics, can be favorably compared to the experimental standard deviation of a series of n measurements of k given by

$$\frac{\sigma_k}{k} = \frac{1}{\bar{k}} \left[\frac{\sum_{i=1}^n (\bar{k} - k_i)^2}{n - 1} \right]^{1/2} \quad (9)$$

The ratio of the value determined by Eq 9 to that by Eq 7 is usually in the range of 1 to 3 and often allows the operator to detect instrumental difficulties. Only one [308] of the 40 computer programs now available for use in quantitative electron probe microanalysis computes the value of σ_k/k (from Eq 7).

Ziebold [137] assumes $B' \simeq B^0 \ll P^0$ (B is not a function of the concentration and a high P/B ratio) and converts Eq 7 to

$$\frac{\sigma_k}{k} = \left[\frac{1}{P^0} \left(\frac{1}{k} + \frac{2B^0}{k^2 P^0} + 1 \right) \right]^{1/2} = \left[\frac{1}{P^0} \left(\frac{1}{k} + \frac{2}{k^2 R} + 1 \right) \right]^{1/2}$$

where R is the peak to background ratio. While significant variations in σ_k/k occur depending on k , R , P^0 , and count time, it is evident from Fig. 44 that a precision well below 1 percent is possible (0.1 percent at 100 s and 0.5 percent at 10 s). To be able to approach in practice this theoretical precision, it is essential to seek out, identify, and minimize the experimental errors. The theoretical precision has been made possible by improvements in the sensitivity (counts per second/beam current) and P/B ratios—through the use of high quality crystals, wider crystal selection, high pressure detectors, improved spectrometer design, and stable instruments. With a goal of less than 0.5 percent for σ_k/k , the significance of the many errors to be discussed will be apparent.

Microanalysis

Specimen Preparation, Coating, and Oxidation/ The specimen surface is of prime importance because electron probe analysis is, to a significant extent, a surface analysis. The range of electrons in solids is generally less than $5\text{ }\mu\text{m}$ and the mean depth of X-ray production (50 percent of the X-ray production is from a lesser depth) is only 27 percent [242] of this range. Consequently, surface problems can have significant effects on the measured intensities. While specimen preparation is to some extent a black art, most metallurgical and geological laboratories can routinely prepare solid specimens using standard metallographic preparation procedures. Specimens are commonly mounted in diethylthallate (low shrinkage, high strength with glass or asbestos) or in epoxy (plexiglass, Epon 512) in the case of heat sensitive materials. For quantitative examination the specimen must be flat, conductive, and representative. Flatness is generally achieved by mechanical polishing with abrasive papers of decreasing coarseness. Fine polishing is achieved with cloth covered wheels impregnated with abrasive compound. A diamond compound (from 6 to $\frac{1}{4}\text{ }\mu\text{m}$) is commonly used, but slurry polishing is useful in the case of softer metals. Attack polishing, chemical polishing, and electropolishing can be utilized in certain troublesome applications. Some specimens including metals, can be successfully prepared for EPA using a microtome.

In preparation, several problems must be avoided or at least recognized.

1. The embedding of polishing compound—We have spent, as have others [309], frustrating hours analyzing SiC , Al_2O_3 , and MgO . The ultrasonic cleaning of a specimen after polishing is recommended.

2. The removal of second-phase material and the subsequent creation of holes, which then are often filled with polishing compound.

3. The generation of relief—Relief can be detected in a metallograph at high magnification prior to inserting the specimen into the instrument. The most difficult means of discerning relief is to rotate the specimen 180° and duplicate the measurements with the same spectrometer (constant efficiency). Many nonexistent concentration gradients near phase boundaries have been reported that were actually a result of relief, which usually increases the take-off angle by effectively tilting the specimen.

4. The rounding of edges during polishing—Many analy-

ses involve investigations at or near the surface of the specimen. Preservation of such edges or surface films in their original state can be a formidable problem. Embedding with epoxy resin (casting or vacuum) or electroless metallic coatings do provide some strength and work well in certain cases. Care must be taken to avoid contamination by the embedding or coating material.

5. Surface smearing—Such smearing is an age-old problem in metallography, which can result in erroneous results, particularly in soft materials, and is usually removed by repeating the polishing and then light etching.

6. Nonflat surfaces—It is generally a simple matter to obtain a flat surface, but nonflat conditions can arise as a result of specimen mounting in the instrument. Figure 45, from Sweatman and Long [284], illustrates the error in the Mg concentration in an olivine due to nonflatness. Flatness is easily achieved in most specimens that can be conventionally polished, but rough or nonflat surfaces cannot be avoided in certain instances—fracture, rolling, heat treatment or processing, corrosion. While high take-off angles minimize the effects of specimen tilt, the problem often reduces to one of recognizing that the specimen is tilted.

7. Scratches—Fortunately, scratches are readily recognized and often can be easily eliminated. Long [147] has reported a 10 percent reduction in the observed Mg concentration (at 15 kV and $\psi = 20^\circ$) in a pyroxene due to localization of the beam in a $0.5\text{-}\mu\text{m}$ -deep scratch. Hallerman and Picklesimer [310] have systematically examined the effects of scratches and other preparation anomalies on EPA measurements.

Specimens for quantitative analysis are not generally chemically etched because of possible component removal, galvanic action, reaction product deposition, and constituent (phase) dissolution. Etching is usually unnecessary because sufficient contrast to delineate phases of interest is available when one of the common imaging capabilities is used. In isolated cases when the contrast is insufficient, for example, in the delineation of grain boundaries, and one must resort to etching, it is recommended that the possible etching effect be studied by specimen mapping with, say, hardness indentations. Microhardness testers that mount on metallograph stages make this a precise, simple, useful procedure. Hallerman and Picklesimer [310] studied the effect of etching Cu-Ni alloys and reported no effect on X-ray emission.

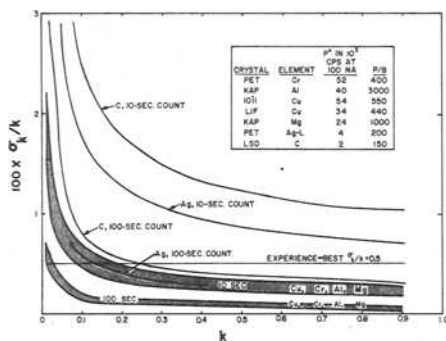


Fig. 44—The theoretical precision in the measured intensity ratio, σ_k/k , as a function of the intensity ratio, k . σ_k/k is calculated from $\sigma_k/k = \left[\frac{1}{P^0} \left(\frac{1}{k} + \frac{2}{k^2 R} + 1 \right) \right]^{1/2}$, where R is the peak to background ratio and P^0 is the number of counts obtained on the pure solute. The values for P/B and P^0 are shown in the legend and were measured experimentally using the indicated crystals. A 100-s counting interval provides good precision as long as $K > 0.1$.

Whenever quantitative results are sought, it is advisable to mount the specimens and all standards in close proximity within the same mount, because (1) if coating is necessary the coating thickness on standard and specimen will be the same, (2) optical refocusing may not be required in moving from specimen to standard if the distance between the two is minimized, and (3) the possibility of contamination from the mounting material is reduced. There are times when it is not possible to achieve this juxtaposition of specimen and standard, as in cases where the standard is costly or rare.

The need for a conductive coating is most pronounced in specimens of low electrical and thermal conductivity in order to prevent charge accumulation and subsequent beam deflection or to prevent thermal damage to the specimen (micro-incineration) or both. Evaporated films of C, Cu, Al, Ni, and Ag from 50 to 400 Å thick are commonly used. The problems associated with such coatings are (1) absorption of the incoming electron beam, which, in effect, lowers the E_0 seen by the specimen; (2) absorption of the emitted X-ray beam; (3) possible fluorescence of the specimen by X-rays generated in the coating or fluorescence of the coating by the specimen; and (4) poor adhesion of the coating. The element used for the coating should be chosen after due consideration of these problems, and the coating should be as thin as possible but still provide the necessary conductivity. Reed [311] has derived an expression for the loss of intensity, ΔI , in percent, due to a film of mass thickness ρz :

$$\Delta I = \frac{83000 \rho z}{E_0^2 - E_c^2} \exp [-(\mu/\rho) \rho z (\csc \psi)]$$

where μ/ρ is the mass absorption co-

efficient and z is the film thickness. Long [147] has reported on the usefulness of this expression.

Whenever possible, coatings should be avoided and in some cases the liberal use of Ag conductive paint will provide the needed electrical conductivity. Some nonconductive specimens (biological thin films, blood, particulate matter) can be successfully studied without coatings by placing them on conductive substrates. Kniseley, Laabs, and Fassel [218] embedded a fine wire mesh in the surfaces of nonconductive specimens that could not be satisfactorily coated by conventional means and did obtain the necessary conductivity.

Intensity fluctuations can appear as a result of conductive coating instability caused by thermal problems, for example, the relative thermal expansion between film and substrate and the generation of volatile substances in the substrate. The problem can usually be overcome by using thicker coatings, altering the choice of coating material, using composite coatings, or operating at lower currents. We have encountered coating instabilities in the analysis of plastics and teeth. An often overlooked problem is that of specimen surface oxidation. Not only is it easily overlooked but it is also sometimes extremely difficult to determine its presence, particularly as the sensitivity for oxygen in most EPAs is low. We have observed the removal of certain oxide films under electron bombardment. Different phases in a multiphase material are often oxidized to different extents. Oxidation effects can be avoided or removed in some cases by polishing just prior to examination, preparation or storage or both in vacuum or protective atmospheres (liquid or gas), and ion bombardment. Once the carefully polished, flat, oxide-free specimen showing no smearing, embedding, or etching effects is mounted, consideration must be given to the errors occurring during analysis.

Carbon Contamination—Its Characteristics and Control/ Carbon contamination of the specimen is a problem common to most electron beam instruments. The presence of residual gases and vapors in the electron column leads to hydrocarbon deposition on the specimen surface, which presumably is decomposed by the electron beam leaving behind a carbon deposit. The deposit manifests itself through (1) a time-dependent decrease in the measured X-ray intensity, (2) a corresponding increase in the $C K\alpha$ X-ray intensity, and (3) a visible dark spot larger than the probe electron beam. Castaing [313] discussed C contamination in 1954 and others [313–316] have pursued it in some detail.

The C film poses several problems. It

absorbs the incoming electrons and reduces the effective E_0 . It absorbs the emitted X-radiation—in studying F in teeth, $(\mu/\rho)_C^{F K\alpha}$ is 6600. These effects are time dependent and hence difficult to correct for in an analytical manner, particularly when attempting to maintain $\sigma_k/k < 0.5$ percent. The deposition of C is dependent on the substrate, and different phases in a given material can be contaminated at different rates. The contamination certainly complicates the analysis of C, particularly when examining low concentration levels (C in Fe) or thin films (biological specimens).

In attempting to characterize the contamination process, we have found that a plot of the rate of contamination as a function of current density in our probe passes through a maximum at about 2 A/cm². At low current densities, below the maximum, deposition processes predominate, while at higher current densities several phenomena may be contributing to the predominance of a C removal mechanism such as specimen heating, ion cleaning, vapor exclusion by the beam, or reaction with gaseous constituents generated in the beam. This relationship between contamination rate and beam current density can qualitatively explain the different appearances of the contamination spot. A gaussian electron beam at low current densities would correspond to maximum deposition at the center, whereas at high current densities (negative slope) maximum deposition would be in the tails of the beam and a contamination ring would be observed. Table 20 illustrates the dependence of the contamina-

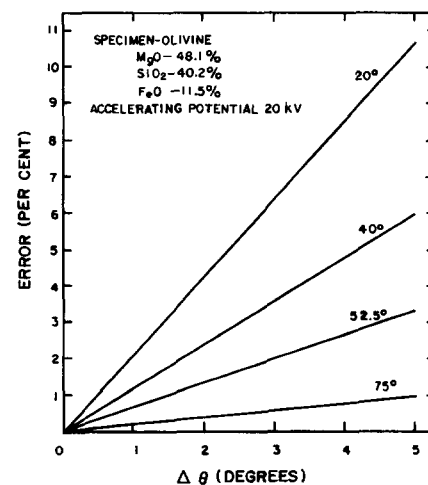


Fig. 45—The effect of unknown specimen tilt on the accuracy of quantitative analysis. The error in the concentration of Mg in an olivine is plotted as a function of the tilt at four different X-ray take-off angles. It is evident that errors of 1 to 3 percent could easily be encountered. Curves from Sweetman and Long [284].

tion rate on the substrate atomic number. Pb has the lowest thermal conductivity. These results are not in accord with those of Gray [317], who found the contamination rate independent of the material.

Many different approaches to the problem of controlling contamination have been attempted. Cold fingers have periodically been utilized to provide a cold surface upon which vapors can condense. The original Cambridge probe (1959) had such a device and another was described in 1970 by Eichen et al [318]. Ruberol et al [315] attached a cold plate to the objective lens, which reduced the contamination rate from 0.7 weight percent C per minute to 0.01 weight percent C per minute. Neuhaus [319] illustrated the effectiveness of large, cooled surface areas in reducing contamination by circulating refrigerant in the water cooling coils of the objective lens in an ARL probe. With Freon the carbon contamination rate on Fe was decreased from about 0.1 weight percent C per minute to less than 0.01 weight percent C per minute. Liquid nitrogen traps on the diffusion pump have generally provided marginal improvement [316]. Molecular sieves in the roughing line (between the diffusion and mechanical pump) reduce the rate significantly. Heating the specimen is effective [315] but can cause physical changes in the specimen such as volatilization, oxidation, phase change, and diffusion. The use of certain diffusion pump oils has been advocated [317]. We have found that the combination of a large, cold surface (cold plate) and a molecular sieve in the roughing line provides satisfactory protection; however, the necessity of heating the cold plate to room temperature before opening the column to air (a 12-min process) is a nuisance.

The use of a controlled gas leak has been suggested [315,320] and it offers the distinct advantage of providing, in addition to the prevention or reduction of contamination, the possibility of cleaning the specimen surface before examination, presumably through ion bombardment. There are several reasons for the lack of use of controlled gas leaks. When oxygen is used oxidation can occur, and we have detected intensity fluctuations in Cu due to alternating formation and removal of a thin oxide film. Originally, investigators encountered difficulty in directing the gas at the point of impingement of the fine electron beam. One manufacturer satisfactorily solved this problem by admitting oxygen to the column in such a manner that it would be directed through the center of the objective pole piece onto the specimen surface. The gas can interfere with the incident beam and reduce the effective acceleration potential. Impure gases can be cleaned by passage through external

Table 20—The Contamination of Pure Materials in an EPA

Target	z	K ¹	Experimentally measured contamination ²	% C contamination per nanoampere per min. ³
Mg	12	.37	5.4%	0.0030
Al	13	.53	5.1	0.0028
Si	14	.20	6.2	0.0034
Fe	26	.18	8.0	0.0041
Cu	29	.94	8.1	0.0041
Ge	32	.14	8.2	0.0041
Ag	47	1.0	9.4	0.0044
Sn	50	.15	9.1	0.0042
Au	79	.71	10.5	0.0045
Pb	82	.08	6.9	0.0029

1) thermal conductivity in cal/cm²/cm/sec/°C; 2) the measured CKα signal as a % of the signal from diamond; measured after 7.5 minutes; 15 kV; i(beam)=210na; 3) corrected for contribution due to backscattered electrons; %C/na/min at a beam current of 210na.

cooling coils, and the leak rate is sufficiently low to not cause degradation in filament life or ultimate vacuum. In a recent article [321] the use of He in a TEM reduced the C contamination rate from 80 Å/min to 19 Å/min. We have found a controlled oxygen leak to be useful in cleaning specimens prior to, but not during, quantitative analysis and in EBS work. Other techniques of avoiding C contamination, such as moving the specimen every few seconds, extrapolating the measured intensity to zero time, or utilizing a high E_0 to reduce the surface contribution to the analysis, are at best of limited value and often negate the usefulness of an electron probe.

Electron Beam Induced Changes in Concentration/ Specimen instabilities can lead to erratic results and incorrect conclusions. In glasses the variations of Na and K [89–92] are well documented. The diffusible ions (Na, K, Cl) in soft tissues or blood can be lost or redistributed under electron bombardment. Volatile compounds such as chlorides can be generated and decomposition may occur. Sr is rapidly volatilized under electron bombardment. Often such instabilities can be detected by observing the emitted X-ray intensity as a function of time. They may be overcome by using thicker conductive coatings, cooling the specimen (which may then become a trap), analyzing thin films (most electrons transmitted), and operating at low currents. The high sensitivity of and EDS can be extremely useful in such cases.

Orientation and Density Effects/ Crystal orientation has been reported to effect X-ray emission through electron channeling in certain directions. A 40 percent decrease in X-ray yield occurred in large single crystals of Cu when the electron

beam was oriented along the [110] direction [322]. Orientation does affect the oxidation characteristics of a material and different grains may exhibit different oxide thickness. It is possible but unlikely that the orientation could significantly affect the contamination rate. Problems due to orientation effects are rarely encountered in practice.

Variations in density can alter the emission. Ranzetta and Scott [313] reported on a graphite specimen with a density of 1.91 g/cm³ that yielded only 85 percent of the intensity observed on pure diamond (3.25 g/cm³). Ichinokawa et al [323] found that the intensity emitted by a specimen depended upon its density. In specimens (C, Cr₂O₃, CuO, ZnS) where the density was varied from 1 to 4 g/cm³ the emission from the low density specimen was only 70 to 80 percent of that from a single crystal. They found that density variations had a negligible effect on $f(\chi)$ and R (backscattered factor) but a significant effect on $F(O)$, implying that the stopping power is the quantity most affected by density variations.

Uncertainty in Standards/ One of the most significant advantages the EPA holds over many other analytical techniques is that pure element standards can often be used in attaining accurate chemical analyses. Since σ_k/k is 0.1 to 0.5 percent at best, an elemental standard 99.9 percent pure is more than sufficient. There are instances when unpure or compound standards must be used, for example, when determining α values for use in the Ziebold and Ogilvie [123] empirical expression, when the pure material is unavailable as a nonvolatile stable solid, and in certain biological and geological applications. When compound standards are used they must be well char-

acterized—accurate chemistry, homogeneous on the micrometer level, nonoxidized, carefully prepared. It is hazardous to use the stoichiometric composition for a compound unless the phase diagram is well established and the compound is prepared under controlled conditions.

Optical versus Spectrometer Depth of Focus/ In most experiments it is necessary to move the specimen and, consequently, the light optics must be refocused, as specimens are often not perfectly flat and stages are not usually perfect. This movement, which causes the source to leave the Rowland circle, can be mitigated by adjusting the optical focus. No serious problems are encountered if the depth of focus of the light optics is less than that of the X-ray spectrometer. Smith and Pedigo [324] examined several crystals and optical objectives in a MAC probe and encountered no problems with either LiF or ADP crystals (relatively low resolution) but did encounter some with KAP. The problem can be minimized by (1) using the lowest resolution crystal that will satisfy the experimental requirements, (2) refocusing both the light and X-ray optics after any specimen translation, and (3) a knowledge of the height sensitivity of each crystal (Fig. 19).

Chemical Inhomogeneity—Is It Real?/ Specimen inhomogeneity is often a problem in EPA which is compounded by the fact that the probe is the only analytical device available that can measure homogeneity on the micrometer level of spatial resolution. Unfortunately, many specimen and instrumental problems cause intensity variations that could be ascribed to specimen inhomogeneities such as oxidation, roughness, contamination, smearing, embedding, subsurface constituents, and focusing uncertainties.

The NBS has systematically examined the homogeneity of certain alloys in their program to generate standards for quantitative EPA, and these publications [309, 325–327] are useful guides to understanding the intricacies of homogeneity determination. Beaman and Schreiber [328] have described a method used by the Midwest Electron Probe Users Group in the screening of alloys for possible group analysis, in which the effects of refocusing and inhomogeneity are isolated. Before studying the homogeneity of an unknown specimen it is advisable to: (1) study the effects of stage motion and optical refocusing in your instrument using a highly polished, flat, pure material; (2) install an anticontamination device; and (3) examine some well characterized materials, such as those supplied by the NBS [309, 325–327, 329].

The Effect of Chemical Bonding on Emission/ The X-ray line wavelength (lo-

cation), shape (asymmetric), and intensity (emission) from an element in a compound often depend upon the chemical bonding of the element. If the state of bonding changes from an unknown to a standard state, the accompanying changes in peak location, shape, and intensity can result in serious errors depending upon the magnitude of the wavelength shift, the peak shape, the resolution of the spectrometer, and the PHA setting.

Sweatman and Long [284] have discussed the problem in detail as it applies to geological samples and have devised a method for making an analytic correction to account for the problem. They discussed the suitability of MgO, Al₂O₃, and SiO₂ as standards in geological applications, as opposed to pure Mg, Al, and Si, and indicated the probability of large errors when K lines for $Z < 18$ and L lines for $Z < 48$ were utilized. In discussing applications, it was illustrated that the magnitude of the shift can be used to good avail in performing quantitative analyses in selected systems where the shift has been measured as a function of composition [214]. The problem may be minimized by always considering the possibility of chemical bonding effects and by readjustment of the spectrometer on standard and unknown whenever possible; however, this will introduce small spectrometer resetability errors and cannot be done easily when the elemental concentration is low. The use of integrated peak areas rather than peak intensities is useful in selected cases but time consuming in the absence of automated data accumulation and reduction. The preferred procedure is to select a standard exhibiting a negligible shift with respect to the unknown.

Spectral Interference and Spectrometer Positioning/ X-ray line interference is not a common problem because of the simplicity of the X-ray spectrum and the abundance of high resolution crystals for wavelengths below 10 Å. The most common and troublesome interferences occur when light elements (B, C, N, O, and F) are being studied in the presence of transition elements. The resolution of the pseudosoap crystals is poor and many of the L lines of the transition element have energies below 1 keV.

Consider, for example, the determination of nitrogen in a steel containing Ti where λ (Ti L _{α}) = 31.4 Å and λ (NK α) = 31.6 Å. The problem is compounded by the fact that low Z elements of interest are often present in low concentrations. Higher order X-ray line ($n > 2$, where $n\lambda = 2d \sin \theta$) interference is easily avoided using energy discrimination (pulse height selection), unless an interfering element is present in high concentration and the analyzed element is present in low con-

centration. For example, in the analysis of F in teeth the high concentration of P (third order K α interference) can cause difficulties [270]. Satellite lines are usually not a problem except in the accurate determination of the background. Possible interferences should be determined before the analysis using tables such as those recently published by White et al [59] or by Heinrich et al [330].

There is a small error associated with spectrometer positioning on the spectral peak. We have found, even with the highest resolution crystal, that the precision in setting the spectrometer by using the rate meter is equivalent to the precision to be expected from Poisson counting statistics; in other words, the reset error in our instrument is negligible when the spectrometer is set manually to maximum intensity by visual observation of a rate meter. There is some degradation of precision when positioning the spectrometer by a dial reading (wavelength, 2 θ reading, specimen to crystal distance). Sweatman and Long [284] suggest positioning the spectrometer with the help of a spectral scan and taking the mean position between the 80 percent maximum intensity positions as the peak location. Repositioning of the spectrometer in an automated EPA is a more complex problem.

Uncertainty in the Acceleration Potential/ Unless the acceleration potential is accurately known, to within ± 200 V, serious errors in the computed concentrations can accrue. When it is possible to measure the high voltage directly, using a precision resistor and probe, it should be done frequently. A less accurate procedure is to plot the intensity (at constant beam current) as a function of potential on the meter and see how close the extrapolation to zero intensity corresponds to E_c for the pure element used as a target. Different elements covering the instrument's useful range of high potential should be used. We have found that an accurate and rapid check on the high potential can be made with an EDS by simply observing the channel number, in a calibrated system, where the continuous background intensity drops to zero.

Drift, Background, and Deadtime/ While the variation of X-ray intensity with time is easy to detect, determination of the cause of the variation may be an exasperating problem. Its solution may prove to be elusive because of the multitude of conditions that can be manifested as intensity drift: variations in any of the power supplies (accelerating potential, lens currents, detector high voltage), stage movement, beam current fluctuation, beam position stability, X-ray spectrometer drift, column vibration, crystal rocking adjustment, filament motion (warpage), changes in detec-

tor gas pressure, temperature changes of the diffracting crystal, electronic counting problems, and specimen difficulties (magnetization, coating instability, volatilization, topography).

In carrying out a drift correction most investigators measure the peak intensity on the standard at the beginning and at the completion of the measurements on the unknown, assume the drift to be linear in time, and use the following expression to make a correction:

$$m_t^0 \text{ (drift corrected)} = m_1^0 + (m_2^0 - m_1^0) (t/\Delta t)$$

where m_t^0 is the standard intensity at time t when the unknown measurement is made, m_1^0 is the standard intensity at the beginning of the experiment when $t = 0$, and m_2^0 is the standard intensity measured after a time interval Δt . Unless some independent experiment has shown the instrument to have linear drift, this approach may be invalid or at best inaccurate. A few authors monitor only the beam or specimen current. This is inadequate since drift in the spectrometer setting, specimen stage (transverse or height), crystal temperature, detector pressure, etc., will not be detected. Monitoring the specimen current is not effective because it varies with the mean atomic number of the target and is, therefore, sensitive to such things as oxide formation or removal, carbon deposition, and subsurface second phases. Topography and pulse amplitude shifts cause intensity variations that could be mistaken for current drift. The best procedure is to have an instrument in which careful measurements of stability have been made and any problems rectified. Then, in the measurement sequence, the standard intensity should be measured frequently and the closest (in time) value used with each unknown intensity to calculate the intensity ratio. Ferguson [331] provides a unique approach to the drift problem encountered in trace analyses requiring long counting intervals.

The following are some of the procedures we have used to isolate or eliminate drift problems. X-ray intensity can be monitored simultaneously on different spectrometers to isolate spectrometer and counting channel variations from other problems. Beam position or stage stability can be studied by positioning the beam directly over an interface (electroplated Cu-Ni couple) and monitoring the X-ray intensity. The magnitude of the beam or stage drift can be determined by driving the specimen at a fixed rate under the beam and plotting the X-ray intensity as a function of position. Knife edges or cylinders can be used in a similar manner. Beam current is easily stabilized by using the feedback current from the objective

aperture to the condenser current supply (see Fig. 2). At one of our laboratories a marked improvement in counting precision was attained by operating after 7 p.m.; hence, all serious quantitative work is performed between 7 p.m. and 1 a.m. All currents (beam, specimen, lens) can be easily monitored and recorded on a strip chart recorder. At the Westinghouse Materials Engineering Laboratory, Lester, Pa., the only way of obtaining the required counting precision was to provide a separate, double-stabilized power line using two stabilizing autotransformers.

The background correction becomes increasingly important as the concentration decreases and the net intensity, $P - B$, diminishes. The most satisfactory correction is the simplest and consists of applying

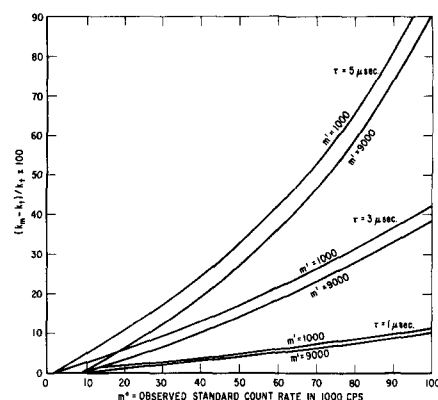


Fig. 46—The relative error, $(k_m - k_i)/k_i$, introduced by neglecting the deadline correction (k_m is the measured probe ratio and k_i is the same ratio after correction for deadline). The relative error in k_i is given as a function of the observed count rate from a standard (m') at two levels of counting on the unknown ($m' = 1000$ and 9000 cps) for three different deadlines ($\tau = 1, 3$, and $5 \mu s$).

the mean of two spectral intensities, one on each side of the peak, with the optimum positions being determined from a spectral scan. There is, however, great interest in calculated background values. In some instances the background intensity in the

analytical line is given by $\sum_{i=A}^N C_i B_i$, where

B_i is the background intensity measured at the spectrometer setting for element i using, as a target, an element with an atomic number close to that of element i . Such a procedure is not always accurate, for example, in using a (1120) quartz crystal, the mean off-peak intensity for Cr K α was 2.1 cps while the intensity from Mn at the Cr angle was 0.7 cps. It is well known that peak to background ratios can vary significantly depending upon the technique used for measuring background.

Some investigators plot B_i versus atomic number or specimen current and then use the observed specimen current or a mean atomic number to calculate the unknown background. The most popular technique is one in which the unknown background intensity, B_A' , is calculated using

$$B_A' = C_A B_A + \sum_{i=B}^N C_i B_i$$

where B_A is the background from a pure target of element A usually measured off spectral peak and B_i is the intensity measured at the spectral peak for element A with a pure i target. Some calculate the background only once using normalized probe ratios for C_i , whereas others calculate it during each iteration using the calculated concentrations for C_i , the latter approach being preferred. The primary reason for the use of these several expressions is the fact that in complex materials interfering spectral lines make it difficult to select an appropriate location for measuring off-spectral peak backgrounds. Recent crystal improvements help to alleviate this problem; nevertheless, the validity of the approximations involved in these expressions needs to be determined experimentally, because in some cases such estimates are necessary (phase analyzer, energy dispersive spectrometers, concentration mapping, geological applications). The most satisfactory correction is obtained when it is possible to measure off-spectral peak intensities in both the unknown and the standard.

A deadline correction should be applied to all measured intensities using the proper expression. Figure 46 illustrates the magnitude of the error introduced by neglecting deadline. Wittry [279], Heinrich et al [71], and Beaman et al [72-74,97] have discussed techniques for measuring deadline in the electron probe. For measured intensities m below 30,000 cps and τ (deadline) values below 3 μs , the Ruark [332] expression, $m/n = 1/(1 + n\tau)$, may be used; however, Beaman, Isasi, and Birnbaum [73,74] have shown that this expression does not always apply. The true counting rate is n .

An investigation [72-74] was carried out to determine the source and nature of deadline in the X-ray counting circuits used in electron probe microanalyzers. The fundamental quantity governing component interaction and, therefore, system counting efficiency is the pulse duration associated with a single counting event. Theoretical expressions governing the behavior of counting systems consisting of two components were derived assuming either nonself-prolonging or self-prolonging behavior for each component. Non-

self-prolonging (nsp) devices are inoperative for a fixed time after activation, and all pulses entering the device during this period are lost to the counting system and have no effect on the initial pulse. Self-prolonging (sp) devices are those in which the incoming pulse interaction results in counting losses and in an output pulse of increased duration. In one experimental study the counting channel components, preamplifiers, amplifiers, and pulse height analyzers (PHA) and scalars were found to be sp, sp, nsp, and nsp, respectively.

Measurements of the triggering sequence, the pulse duration characteristic of each component, and the nature of each component, coupled with the theoretical expressions governing component interaction, led to the conclusion that many commercial counting chains could be reduced to two-component systems consisting of an sp amplifier with pulse duration τ and an nsp PHA with pulse duration λ . Experimental measurements of system losses for $\tau > \lambda$ revealed that the efficiency was given by $m/n = e^{-n\tau}$. In this case, the deadtime was τ' , where $\tau' = (e^{n\tau} - 1)/n$. When $\lambda > \tau$, the efficiency was found to be $m/n = 1/\{e^{n\tau} + n(\lambda - \tau)\}$ and the system deadtime was $(\tau' + \lambda - \tau)$. Approximate expressions such as $n = m(1 + m\tau)$ should not be used.

The Analytical X-ray Volume/ A troublesome situation often arises in the analysis of fine microstructures. Here it is possible for the excited X-ray volume to penetrate the constituent being analyzed because of the irregular shape or to have the excited volume extend into a sub-surface constituent. The problem can often be anticipated if the areas to be analyzed are carefully studied in the EBS mode

using specimen current prior to the collection of a large number of quantitative data. It is advisable to have a good idea of the size of the excited X-ray volume, and the liberal use of a variety of undiffused couples is suggested in addition to reference to the curves in Fig. 11. The nomogram in Fig. 47, published by Reed [43], is a useful guide. Whenever complex microstructures are studied, the X-ray emission behavior of a particular phase should be duplicated on several different particles.

Base Line Clipping/ Base line clipping, described by Heinrich et al [71], is caused by a reduction in pulse amplitude at higher intensities [66-68], presumably due to detector anode wire contamination [69,70]. The clipping occurs when the amplitude reduction is such that some pulses in the distribution have amplitudes less than the base line voltage. Pulse amplitude shift can be substantially reduced by placing the entire detector assembly in an evaporator [70], as shown in Fig. 48, and cycling the wire between red and white hot for 60 min. This extremely effective procedure was suggested by Lifshin [96].

Know Your Instrument and What Precision to Expect/ It is imperative that any analyst know and periodically determine S for his instrument; here S is the ratio of Eq 9 to Eq 7,

$$S = \frac{1}{k} \left(\frac{\sum_{i=1}^n (\bar{k} - k_i)^2}{n-1} \right)^{1/2} / \left(\frac{P' + B'}{(P' - B')^2} + \frac{P^0 + B^0}{(P^0 - B^0)^2} \right)^{1/2} > 1$$

S values for today's instruments generally lie in the range of 1 to 3 and any value over 2.5 usually indicates the presence of a correctable condition. Ziebold [137] showed several years ago that one reason for large S values was the difficulty in maintaining simultaneous optical and X-ray focus. In our instruments we have found that increased counting times up to 600 s improve the precision but beyond that no significant improvement is obtained.

While it takes considerable care and knowledge to generate accurate k values, it can be done rapidly on a routine basis by an experienced analyst. The precision obtained in k values measured on inter-laboratory studied specimens by the Midwest Electron Probe Users Group has improved from 10 to 20 percent on the first specimens studied to 1 to 5 percent in the four years it has performed quantitative analyses. In our own laboratories our best effort consists of having two analysts measure three k values per specimen on three different days. For these 18 k values,

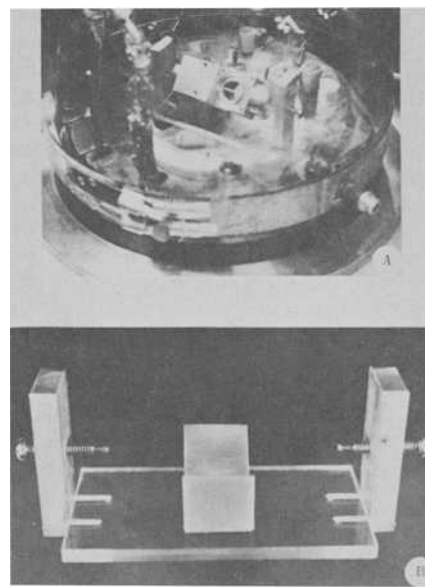


Fig. 48—A technique for cleaning the anode of a proportional detector without removing it from the detector: (a) the detector in the evaporator with the anode white hot and (b) the mounting for holding the detector assembly.

when $k > 10$ percent σ_k/k is generally less than 1 percent (0.5 to 1 percent) and for 1 percent $< k < 10$ percent σ_k/k is usually 1 to 3 percent.

What one does with such accurate k values is a matter of choice. Very few analysts today assume $k = C$ or let the normalized k values represent the actual chemical composition. Some make simple corrections by hand [7,333]. Others attempt the more accurate but time consuming task of calculating concentrations by hand using a complete quantitative correction scheme, in which case computation errors in multicomponent systems are inevitable. The masochist takes off a year and writes and debugs a complete computer program for converting his k values to actual composition values. The affluent investigator submits his data for computation to some pay service [334]. The wise investigator fortunate enough to have in-house computing facilities uses one of the 40 published programs readily available for his use. The basis of these programs and the procedure for converting k values to C values is discussed in the following section on quantitative analysis.

Quantitative Analysis

The conversion of experimentally observed X-ray intensity ratios, k , into true chemical compositions, C , has perhaps received more attention than any other single aspect of electron probe analysis. Many papers are published on this subject and interest is keenest in this area at EPASA national meetings. This is not surprising

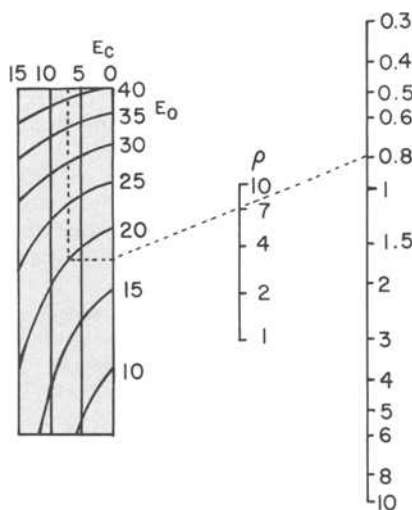


Fig. 47—A nomogram for calculating the qualitative X-ray resolution. The analysis of Fe ($E_c = 7.1$ keV) at 20 keV in a specimen with a density of 7 g/cm³ is illustrated. A qualitative X-ray resolution of 0.8 μ m is predicted. Nomogram from Reed [43].

when the possibility of the accurate chemical analysis of a cubic micrometer of matter using simple, pure element standards, which represents a great advance in the analytical chemistry of a myriad of materials, is considered. In this section a brief discussion of the analytical expressions will be followed by a thorough example problem.

Such a presentation is included in this review for the following reasons. (1) While we cannot deny that those intimately involved in the theory of quantitative analysis will gain little from such presentation, many analysts simply use published expressions and do not have the time to pursue the theory in great detail. Hopefully, this discussion will provide some understanding of the expressions being used and give some intimation why the present accuracy is often not as good as desired. (2) Many investigators find themselves faced with the need to convert k to C values as a result of the addition of an EDS to a SEM. This discussion should be most useful to those microscopists suddenly confronted with a formidable amount of literature concerning quantitative analysis. (3) Finally, some analysts still avoid the use of the quantitative correction because of the aura of complexity and conflict often encountered at national meetings or in the literature. As has been shown, electron scattering and energy losses in solids are complex phenomena, and it is this complexity that limits the accuracy and range of applicability of the commonly used correction models. However, the expressions commonly used to describe these processes are not complex. It is well to keep in mind that, while physicists have been studying this problem for many years, the number of good experimental data in the range of energies encountered in EPA are limited, primarily because the critical experiments are difficult to carry out. Our aim here is to indicate that the development of an overall correction scheme is straightforward and that the use of the scheme is simple but, nonetheless, wearying.

The derivation of the individual analytical expressions will be bypassed because of space limitations, but we will discuss the origin of the individual corrections and their combination into a total correction scheme, present the analytical expressions, show how to use them correctly, and provide all of the data required to carry out a hand calculation. We hope to stimulate the uninitiated to use these quantitative expressions with understanding and confidence.

The Origin of the Four Corrections/ Before developing the general correction equation, we shall consider the individual corrections that are encoun-

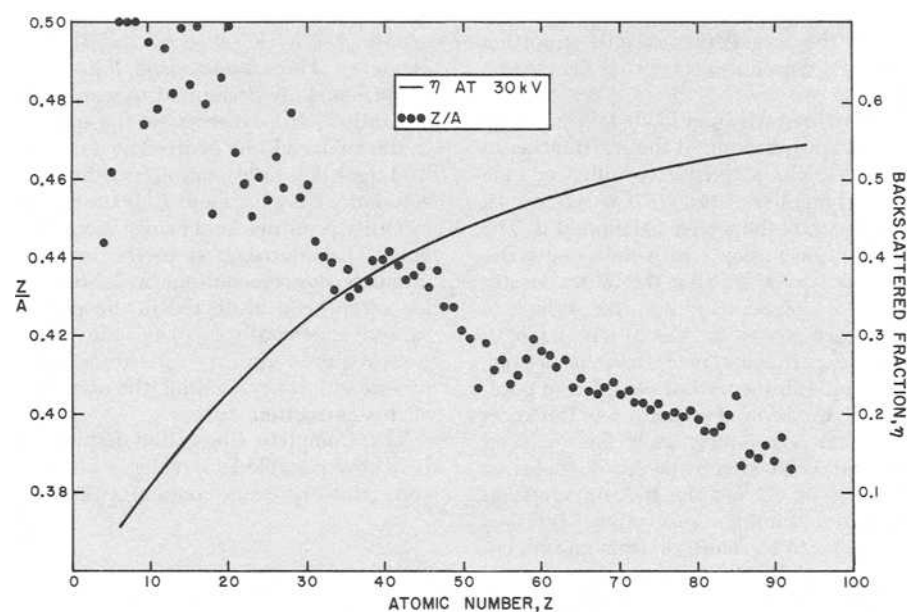


Fig. 49—On the left-hand axis, Z/A is plotted as a function of atomic number Z ; A is the atomic weight. On the right-hand axis, the backscattered electron fraction is plotted as a function of atomic number. η is the ratio of the number of backscattered electrons to the number of incident electrons. The η versus Z data at 30 kV from H. Bishop [335].

tered. In this discussion the average behavior of a group of electrons will be considered rather than the fate of individual electron trajectories as is done in the Monte Carlo calculations discussed later. In addition, it will be important to continuously distinguish between X-radiation *generated within* the specimen and X-radiation *emitted by* the specimen, the latter usually being the smaller of the two.

The need for correction arises because the behavior of X-rays and electrons is different in each material, causing the behavior in an unknown material to differ from that in a standard. Electrons of sufficient energy, upon penetrating matter, will generate X-radiation as a result of energy loss (dE/dx). Recall that dE/dx is the energy loss per unit path length of electron trajectory, x ; $1/\rho (dE/dx)$ is defined as the stopping power, S , of the material for electrons; and ρ is the density of the material. S determines the mass penetration, ρx , of the electrons in the target along the electron trajectory and is referred to as the *penetration or stopping power or energy loss correction*. Electrons that are scattered from the incident direction by more than 90 deg can escape from the target if such scattering occurs close enough to the target surface. To the extent that these electrons have energies in excess of the excitation potential of the element being analyzed, there is a loss of generated X-radiation. This correction is referred to as the *backscattered electron correction R*. The combination of the backscattered electron correction and the energy loss correction

S is referred to as the *atomic number or generation correction*. As will be shown later, the energy loss is proportional to the number of electrons per unit mass, that is, Z/A . Because Z/A decreases with increasing atomic number, although not smoothly (see Fig. 49), the lower the mean Z of the target is, the greater the energy loss for unit ionization and the smaller the amount of X-ray generation. On the other hand, the loss of electrons through backscattering increases with the mean atomic number (Fig. 49); hence, the lower the Z the smaller the backscatter loss and the greater the amount of X-ray generation. This means that there is a tendency for the R and S effects to compensate for each other's corrections so that often the atomic number correction, Z , will be small or negligible. This compensation led to a stimulating controversy over the existence of an atomic number effect in the early days of quantitative analysis. Analytical expressions for R and S are used to obtain a value for the number of photons generated per incident electron.

Next it is necessary to correct for absorption effects in the target, since the generated X-ray intensity is attenuated upon leaving the target. The extent to which any X-radiation is absorbed depends upon the absorption path length, the composition of the material intervening between the source and the target surface, and the energy of the emitted radiation. Hence, not only do we need to know the number of photons provided by the Z correction but we also need to know how

those photons are distributed in depth within the target, that is, only a portion of the total excitation occurs at the target's surface.

A few investigators [336–339] have experimentally measured the distribution in depth of characteristic X-radiation in a limited number of targets (Cu, Al, Au, Ti, Pb); several others have calculated it. The distribution in depth of X-radiation is defined as $\phi(\rho z)$ where ρ is the target density and z is the depth below the surface of the target and not the electron path length x . The experimental measurements of $\phi(\rho z)$ are simple in theory but complex in practice. A thin layer of element B of thickness dz on an A substrate (A is the analyzed element) is covered by layers of increasing thickness of A, and the B X-ray emission measured through successive layers is compared to the emission from an isolated thin film of B. The ratio of the measured intensity of B from the sandwich target (after correction for absorption by A and continuous fluorescence excitation) to that emitted by the isolated thin film is $\phi(\rho z)$ for a mass depth ρz .

A plot of $\phi(\rho z)$ versus ρz is shown in Fig. 50. There, the distribution in depth reveals that $\phi(\rho z)$ at the surface, $\phi(0)$, is greater than unity because of excitation by electrons backscattered from the underlying block. $\phi(\rho z)$ increases initially, because, as electron scattering is established, the distance traversed by an electron in a given interval of depth increases and the greater path length dx in thickness dz means more ionization. Finally a point is reached where the path length becomes constant and the travel of the electron becomes random; this is called the *depth of complete diffusion*. Once this point is reached, the emission depends only on the number of electrons reaching that depth and the decrease in $\phi(\rho z)$ is identical to the absorption of electrons by the target. Once the distribution in depth is known, it must be corrected for absorption, which is done using Beers' law for X-ray absorption:

$$I(\text{transmitted}) = I(\text{incident}) \times \exp[-(\mu/\rho)\rho x]$$

where I is the intensity, μ/ρ is the mass absorption coefficient, and x is the path length. This *absorption correction*, A , constitutes the predominant correction in quantitative microanalysis.

X-radiation can be produced in a target not only by the incident electron beam (primary radiation) but also by other X-radiation (secondary fluorescence). In a composite target any X-radiation with energy in excess of the excitation potential of the analyzed element can generate additional intensity in the analyzed line. The exciting radiation can be either another characteristic X-ray line or X-radiation

from the continuous spectrum when λ (exciting) $< \lambda$ (K, edge of the analyzed element). The *characteristic fluorescence correction*, F , is performed by calculating the ratio I'_f/I_p' , where I'_f is the intensity in the analyzed line emitted by a composite target due to excitation by other characteristic X-ray lines and I_p' is the emitted intensity resulting from primary excitation only. The contribution to the measured intensity due to continuous fluorescence has often been neglected in the past because it is generally small and the calculations required are involved. More will be presented later concerning the magnitude of this correction.

The Complete Correction Expression/ It is now possible to develop a complete correction expression containing these four

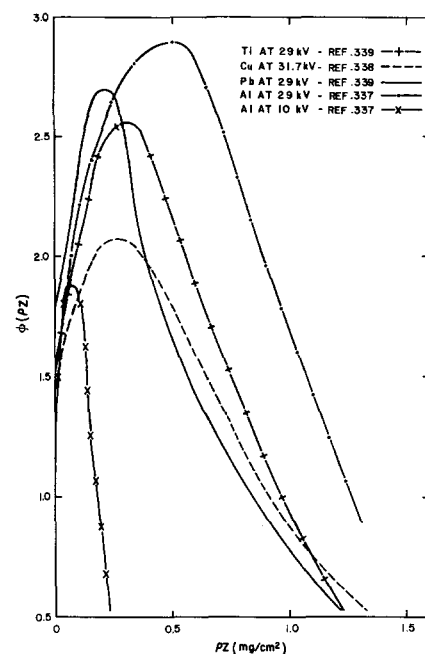


Fig. 50—The experimental distribution in depth of primary X-radiation, $\phi(\rho z)$, is plotted as a function of ρz for Al, Ti, Cu, and Pb. The Al data at 10 and 29 kV, from Castaing and Henoc [337], were obtained with a Mg tracer. The Ti and Pb data at 29 kV, from Vignes and Dez [339], were obtained with V and Bi tracers for Ti and Pb, respectively. The Cu data at 31.7 kV, from Shimizu et al [338], were obtained with a Zn tracer.

effects— $\bar{Z}$, A , F , and continuum fluorescence. The generated X-ray intensity is obtained by integrating the experimental distribution in-depth function over the total effective depth,

$$I_g^0 = \int_0^{z^*} \phi(\rho z)^0 d(\rho z)^0 \quad (10)$$

The superscripts, prime and zero, will denote the unknown and pure standard, respectively; z represents the depth normal to and below the surface of the target; A

will represent the analyzed element and B, C, . . . , N the other elements in the system; z^0 is the mean depth below the target surface at which the average energy of electrons equals the excitation potential of element A.

To relate the generated intensity to the total emitted intensity, the correction for absorption is applied. The absorption path length is $z/\sin \psi = z \csc \psi$, where ψ is the X-ray take-off angle. The emitted intensity is then the integrated product of the generated intensity and $\exp[-(\mu/\rho)\rho z(\csc \psi)]$ at each depth.

$$I_e^0 = \int_0^{z^*} \phi(\rho z) \exp \{[-(\mu/\rho)\rho z(\csc \psi)]\} d(\rho z) \quad (11)$$

To obtain the actual value of the measured intensity, I_e^0 would have to be multiplied by the spectrometer efficiency and the included solid angle $\Omega/4\pi$, where $\Omega = (\text{effective crystal area})/(\text{target to crystal distance}, r)^2$. However, as will be shown later, when using ratios these factors drop out. To obtain emitted and generated X-ray intensity ratios, assume that the characteristic A radiation generated in an A, B, . . . , N alloy, in a layer of thickness $d(\rho z)$, is $C_A \phi(\rho z)' d(\rho z)$.

$$\text{Let } \chi' = \sum_{j=1}^n C_j (\mu/\rho)_j^A \csc \psi. \text{ For an A,}$$

B, . . . , N alloy, χ' is simply the product of $\csc \psi$ and the mass absorption coefficient representing the absorption of A X-radiation by the composite target, that is, $\chi' = (\csc \psi) \{(\mu/\rho)_A^A C_A + (\mu/\rho)_B^A C_B + \dots + (\mu/\rho)_N^A C_N\}$, where $(\mu/\rho)_j^A$ is the mass absorption coefficient for A X-radiation (emitted) by j (absorber). The ratio of the emitted intensity from an alloy I_e' to that emitted by a pure standard is defined as k_e , where

$$k_e \equiv \frac{I_e'}{I_e^0} = \frac{C_A \int_0^{z^*} \phi(\rho z)' \exp(-\chi' \rho' z) d(\rho z)'}{\int_0^{z^*} \phi(\rho z)^0 \exp(-\chi^0 \rho^0 z) d(\rho z)^0} = C_A \frac{F(\chi)'}{F(\chi)^0} \quad (12)$$

χ^0 is $(\mu/\rho)_A^A (\csc \psi)$. Since measurements on the unknown and the standards are made with the same spectrometer, the $\Omega/4\pi$ and spectrometer efficiency factors drop out. The integrals for the alloy and standard materials are defined as $F(\chi)'$ and $F(\chi)^0$, respectively, and can be evaluated numerically when experimental $\phi(\rho z)$ versus ρz data become available.

In the absence of absorption ($\chi' = \chi^0 = 0$) the ratio of generated intensities k_g is given (from Eq 12) by

$$k_g \equiv \frac{C_A \int_0^z \phi(\rho z)' d(\rho z)'}{\int_0^z \phi(\rho z)^0 d(\rho z)^0} = C_A \frac{F(0)'}{F(0)^0} \quad (13)$$

Substituting $k_g F(0)^0/F(0)'$ for C_A in Eq 12 provides a useful relationship between k_g and k_e ,

$$k_e = k_g \frac{F(0)^0}{F(0)'} \frac{F(\chi)'}{F(\chi)^0} = k_g \left(\frac{f(\chi)'}{f(\chi)^0} \right) \quad (14)$$

Here $f(\chi)$ is defined as the fraction of the generated intensity that is emitted, $f(\chi) \equiv F(\chi)/F(0)$. Then k_e and C are related by

$$k_e = C_A \left(\frac{F(0)'}{F(0)^0} \right) \left(\frac{f(\chi)'}{f(\chi)^0} \right) \quad (15)$$

The first term in brackets is referred to as the atomic number factor $\bar{Z}$, because it deals purely with the difference in generation of X-radiation in the unknown and standard; the second term is referred to as the absorption correction A, because it deals with the reduction of the generated intensity due to target absorption.

Next consider the effects of secondary fluorescence. Let I_p , I_f , and I_{cf} be the emitted A X-radiation due to excitation by the primary electron beam, excitation by other characteristic X-ray lines, and excitation by the continuous X-ray spectrum, respectively. I_t is the total emitted X-ray intensity. k_e , previously defined, is

$$k_e = \frac{I_p'}{I_p^0} = \frac{I_t' - I_f' - I_{cf}'}{I_t^0 - I_f^0 - I_{cf}^0} \quad (16)$$

Let $k_1 \equiv I_{cf}'/I_{cf}^0$, $k_2 \equiv I_f'/I_f^0$, and $\gamma \equiv I_f'/I_p'$, then the experimentally observed intensity ratio corrected for dead-time, background, and drift is k , where $k = I_t'/I_t^0$.

Background radiation is made up of continuum radiation, stray radiation, interfering lines, and high-order diffraction lines. In most cases only the first is significant. Dividing the numerator and denominator of Eq 16 by I_t^0 gives

$$k_e = \frac{I_p'}{I_p^0} = \frac{I_t'/I_t^0 - (I_{cf}'/I_{cf}^0)(I_f^0/I_t^0) - \left\{ \frac{I_f' I_p'}{I_p^0 I_t^0} \right\}}{1 - (I_{cf}^0/I_t^0)} \quad (17)$$

or, using the expressions defined above,

$$k_e = \frac{k - k_1 k_2 - \gamma k_e (I_p^0/I_t^0)}{1 - k_2} \quad (17)$$

Writing I_p^0/I_t^0 as $(I_t^0 - I_{cf}^0)/I_t^0$, which equals $(1 - k_2)$, gives

$$k_e = \frac{k - k_1 k_2 - \gamma k_e (1 - k_2)}{1 - k_2}$$

or

$$k_e = \frac{k - k_1 k_2}{(1 - k_2)(1 + \gamma)} = C_A \left(\frac{F(0)'}{F(0)^0} \right) \left(\frac{f(\chi)'}{f(\chi)^0} \right) \quad (18)$$

Solving for C_A in terms of k gives

$$C_A = \frac{k - k_1 k_2}{1 - k_2} \left(\frac{F(0)^0}{F(0)'} \right) \left(\frac{f(\chi)^0}{f(\chi)'} \right) \left(\frac{1}{1 + \gamma} \right) \quad (19)$$

In the absence of continuum fluorescence effects, $k_2 = 0$ and we obtain the familiar correction expression

$$C_A = k_A \left(\frac{F(0)^0}{F(0)'} \right) \left(\frac{f(\chi)^0}{f(\chi)'} \right) \frac{1}{1 + \sum_{j=B}^N \gamma_j^A} \quad (20)$$

Note that γ must be obtained for each possible case of characteristic fluorescence, the fluorescence of A by B, A by C, . . . , and A by N, and the effect summed. The three terms in brackets represent, respectively, the atomic number $\bar{Z}$, the absorption A, and the characteristic fluorescence effects F . This leads to the commonly used terminology $C_A = k_A \bar{Z} A F$ and reference to $\bar{Z} A F$ schemes. The need for correction and the magnitude for each of the $\bar{Z} A F$ factors are illustrated in Table 21. Note that in the simple Al-Mg binary a measured Al intensity ratio of 2.6 percent corresponds to a chemical concentration of 10 percent Al.

Absorption Correction/ The next step is to obtain analytical expressions for the correction functions. We have seen already that $F(0)^0$ and $F(\chi)^0$, and, hence, $f(\chi)^0$ can be evaluated by numerical integration of experimental $\phi(\rho z)^0$ data, of which there is a limited supply. Very few $\phi(\rho z)'$ experimental data are available. Philibert [340] derived an expression for $f(\chi)$ in 1962 and by fitting it to the experimental data available at that time [336] he was able to obtain an expression useful over a wide range of atomic numbers and acceleration potentials. Philibert [340] proposed

$$f(\chi) = \frac{1 + h}{\left(1 + \frac{\chi}{\sigma}\right) \left(1 + h \left(1 + \frac{\chi}{\sigma}\right)\right)} \quad (21)$$

$f(\chi)^0$ is evaluated using h^0 and χ^0 and $f(\chi)'$ using h' and χ' .

Philibert's σ value, which was a function of acceleration potential only, has more recently been replaced by a form suggested by Duncumb and Shields [117] which includes the excitation potential of the element being analyzed,

$$\sigma = \frac{C \times 10^5}{E_0^n - E_c^n} \quad (22)$$

Different values of C and n have been proposed by several authors (C is followed by n within the parentheses): Duncumb and Shields (1.39, 1.5) [117], Heinrich (4.25, 1.67) [116], Andersen (2.39, 1.68) [242], Belk (5.28, 1.7) [341], and Heinrich (4.5, 1.65) [342]. Duncumb et al [120] have studied 450 binary alloys and silicates and recommend that the latter values be used and that no further improvement is to be expected by varying C and n . Beaman [126], Boyd et al [343], and Sweatman and Long [284] all report improvements when using the Heinrich [342] values instead of those originally proposed.

Philibert [340] defined $h \equiv 1.2A/Z^2$. h^0 is $1.2A(A)/Z^2(A)$. Most authors obtain h' from a weighted composition average of h values for the individual components,

$$\text{i.e., } h' = \sum_{i=1}^n C_i h_i. \text{ Some time ago Beaman}$$

[344] studied the effect of using atomic fractions, a_i , in place of weight fractions

$$\left(h' = \sum a_i h_i \text{ or } h' = \frac{1.2 \sum a_i A_i}{\sum (a_i Z_i)^2} \right)$$

and found that, while the different expressions can lead to considerably different values for h' in systems where a_i and C_i differ significantly, the effect on the absorption correction was generally negligible because $f(\chi)$ is not very sensitive to Z .

Beaman [344] concluded that the differences between the expressions were usually inconsequential and recommended the latter expression in cases where C_i and a_i differed markedly. Andersen [283] and Reuter [345] also recommended using atomic fractions. The absorption correction then can be performed using the expressions

$$f(\chi)' = \frac{1 + h'}{\left(1 + \frac{\chi'}{\sigma}\right) \left(1 + h' \left(1 + \frac{\chi'}{\sigma}\right)\right)} \quad (23)$$

and

$$f(\chi)^0 = \frac{1 + h^0}{\left(1 + \frac{\chi^0}{\sigma}\right) \left(1 + h^0 \left(1 + \frac{\chi^0}{\sigma}\right)\right)} \quad (24)$$

where

$$\begin{aligned} \chi^0 &= (\mu/\rho)_A^A \csc \psi, \\ \chi' &= \csc \psi \{ (\mu/\rho)_A^A C_A + (\mu/\rho)_B^A C_B \\ &\quad + \cdots + (\mu/\rho)_N^A C_N \}, \\ h^0 &= 1.2A(A)/\{Z(A)\}^2, \\ h' &= h^0(A)C_A + h^0(B)C_B \\ &\quad + \cdots + h^0(N)C_N, \text{ and} \\ \sigma(A) &= 4.5(10^5)/\{E_0^{1.65} - E_c(A)^{1.65}\}. \end{aligned}$$

The absorption correction is given by $f(\chi)^0/f(\chi)'$ and is usually the largest of all the corrections because the alloy absorp-

Table 21—The Magnitude of the ZAF Factors in Three Example Systems

System: Inclusion analysis in commercial Si at 15 kV with $\psi=18^\circ$ ¹ .							
Element	k(expt) wt.%	Correction factors ²				C(calc) wt.%	
		Z	A	F	ZAF		
Si	38.6	0.922	1.441	1.000	1.329	51.3	
Ti	6.7	1.091	1.064	0.978	1.135	7.6	
V	15.7	1.121	1.042	0.998	1.166	18.3	
Cr	17.6	1.106	1.047	0.997	1.155	20.3	
Fe	2.6	1.116	1.095	1.000	1.222	3.2	
Total	81.2					100.7	

System: Al concentration in four Mg-Al binary alloys; ³ 15 kV with $\psi=18^\circ$.							
Element	k(calc) wt.%	Correction factors ²				C(true) wt.%	
		Z	A	F	ZAF		
Al	0.23	1.031	4.115	1.000	4.242	1.0	
Al	1.22	1.030	3.968	1.000	4.086	5.0	
Al	2.58	1.029	3.774	1.000	3.882	10.0	
Al	5.74	1.026	3.401	1.000	3.488	20.0	
Mg	79.36	.994	1.017	0.997	1.008	80.0	
Total	85.10					100.0	

System: The composition of the bonding and periclas phases in a brick sample; ¹ 10 kV at $\psi=18^\circ$ ⁵ .							
Element	k(expt) ⁴ wt.%	Correction factors ²				C(calc) wt.%	wt.% oxide
		Z	A	F	ZAF		
Mg ⁶	0.50	.999	.922	.999	.920	0.46	0.7
Al ⁶	0.02	.999	.909	.996	.905	0.02	0.04
Si ⁶	17.20	.999	.913	.999	.912	15.67	33.5
Ca ⁶	48.10	.998	.980	1.000	.979	47.08	65.9
Total	65.82					63.23	100.1
Mg ⁷	59.60	1.000	1.002	1.000	1.002	59.73	99.0
Al ⁶	0.10	1.043	1.395	1.000	1.453	0.14	0.3
Si ⁶	0.04	1.043	1.244	1.000	1.297	0.05	0.1
Ca ⁶	0.04	1.046	0.999	1.000	1.045	0.05	0.1
Total	59.78					59.97	99.5

1) Actual experimental systems and data; 2) Z =atomic number correction= $F(0)^0/F(0)'$, A =absorption correction= $f(\chi)^0/f(\chi)'$, F =characteristic fluorescence correction= $1/(1+\Sigma\gamma)$, $C(\text{calc})=k(\text{expt}) \cdot (ZAF)$; 3) assumed composition used to calculate intensity ratio; 4) k here is $\{(P'-B')/(P''-B'')\} \times C''$ where the double prime superscript refers to a mineral standard; 5) in this analysis oxygen is an unmeasured element which is computed by difference and all elements are assumed oxidized; 6) Hess 39 standard; 7) MgO standard.

tion coefficient, $(\mu/\rho)_{A\ldots N}^{K\alpha}$, can be many times larger than the self-absorption coefficient, $(\mu/\rho)_A^{K\alpha}$.

Figure 51, from Yakowitz and Heinrich [346], clearly illustrates that large errors can be encountered in the absorption correction due to uncertainties in the mass absorption coefficient, acceleration potential, and take-off angle. The relative error in $f(\chi)$, $\Delta f/f$, is plotted as a function of the mass absorption coefficient of the target. If the errors in the experimental probe ratio, the atomic number correction, and the characteristic fluorescence correction were negligible and $\Delta f^0/f^0 \ll \Delta f'/f'$, as is often the case, then $\Delta f/f \approx \Delta f'/f' \approx \Delta C/C$. In the Yakowitz and Heinrich calculations the Heinrich modification [342] of the Duncumb and Shields expression for σ [117] is used in the Philibert [340] expression for $f(\chi)$. The plotted errors are

due to a modest relative error in μ/ρ of 5 percent, a large error in the take-off angle of 1 deg, and a small error in the acceleration potential of 250 V. The large errors point out the need for good μ/ρ data and an accurate knowledge of ψ and E_0 . The advantages of low potential and high take-off angle operation are evident. Unfortunately, in existing instruments ψ is fixed and some instruments do not function well at low voltage (<10 kV).

Table 22 was extracted from curves used in another paper by Yakowitz and Heinrich [347] which discussed in detail the errors in $f(\chi)$ for Al in a 50Al-50 Mg alloy, a system with a large absorption correction. The magnitude of the errors is not dependent upon the model selected for evaluating $f(\chi)$, but the values of $f(\chi)$ are and significant variations are found at low $f(\chi)$ values.

There are advantages to a low ψ which can be of practical use in some cases. In the analysis of fine structure (inclusions, eutectoid structures, etc.), where secondary fluorescence is a possibility, it is best to restrict the analysis to as shallow a depth as possible. The errors introduced by the excitation of secondary radiation below the phase of interest are minimized by a long absorption path length. The effective analytical depth is simply the quotient of the target thickness necessary to lower the fluorescent radiation to an insignificant value and $\csc \psi$. When continuous fluorescence is a problem, the errors in the analysis of small particles (near phase boundary) are less at smaller ψ .

Characteristic Fluorescence Correction/ Consider now the characteristic fluorescence correction. Reed [118] has modified the original expression for γ

proposed by Castaing [4] in 1951 into the form widely used today:

$$\frac{I'_f}{I_p} = \gamma = 0.5P_{ij} \frac{r(A) - 1}{r(A)} \omega(B) \frac{A}{B} (\mu/\rho)_A^B$$

$$(X + Y) \left(\frac{U(B) - 1}{U(A) - 1} \right) C_B^{1.67} \quad (25)$$

where $r(A)$ is the absorption edge jump ratio for the analyzed element, A, that is, the element being fluoresced by element B; $\omega(B)$ is the fluorescence yield for the fluorescing element B; A = atomic weight of element A; B = atomic weight of element B; $(\mu/\rho)_A^B$ is mass absorption coefficient of the element being fluoresced by the fluorescing radiation; $U(B) = E_0/E_c(B)$; $U(A) = E_0/E_c(A)$; and C_B = concentration of the fluorescing element.

$$X = \frac{\ln \left(1 + \frac{\chi'(A)}{\chi'(B)/\csc \psi} \right)}{\chi'(A)}$$

$$Y = \frac{\ln \left(1 + \frac{\sigma}{\chi'(B)/\csc \psi} \right)}{\sigma}$$

$\chi'(A)$ is χ' evaluated for A X-radiation and $\chi'(B)$ is χ' evaluated for B X-radiation.

P_{ij} (i excites j), which is used to allow for other than KK fluorescence, appears because, in deriving the expression for γ , the ratio of the primary intensities, I_i/I_j , is encountered. Reed [118] measured I_L and by comparing it with calculated values obtained $P_{KK} = P_{LL} = 1$, $P_{LK} = 4.2$, and $P_{KL} = 0.24$. Heinrich [116] has suggested that P_{LK} should be 2.4, while Brown and Criss [348] confirmed the 4.2 value. Further experimental work is in progress. Reed uses the σ values proposed by Philibert [340] in the calculation of Y . Since there are no fitting parameters in the expression for γ and Y involves the absorption of the fluorescing radiation, σ should be given by $4.5 \times 10^5 / (E_0^{1.65} - E_c(B)^{1.65})$. Heinrich and Yakowitz [349] found that a 20 percent error in σ resulted in an absolute error of less than 0.1 percent Fe in a 10 Fe-90 Ni alloy. Consequently, the selection of σ is not of great practical importance. The variation of the error with E_0 due to a 20 percent error in σ is also negligible.

γ must be calculated for each fluorescing element in the system, that is, for A radiation fluoresced by B radiation, by C radiation, . . . , and by N radiation. Thus, γ is written

$$\gamma_A = \sum_{j=B}^N \gamma_j^A$$

with $\gamma_j^A = 0$ when element j does not fluoresce element A. It is common in KK fluorescence to assume that the fluorescing radiation is all $K\alpha_1$ radiation and neglect the fact that about 10 percent of the

fluorescing radiation is $K\beta$, thereby introducing some error into the calculation of $\chi'(B)$; Reed [118] finds this effect generally negligible. Correction for fluorescence by $K\beta$ radiation in the absence of $K\alpha$ excitation is allowed for by multiplying γ_j^A by 0.1, the fraction of K intensity in the $K\beta$ line; $(\mu/\rho)^{K\beta}$ should be used in the calculation of $\chi'(B)$ and for $(\mu/\rho)_A^{BK\beta}$. For LL and LK fluorescence, where $L\beta$ excitation is possible in the absence of $L\alpha$ excitation, Reed multiplies γ_j^A by 0.4.

The absorption jump ratio $r(A)$ is the ratio of the maximum μ/ρ to minimum μ/ρ at the absorption edge of element A. The jump ratios can be calculated from the data of Heinrich [350] since $\mu/\rho = C\lambda^n$. Heinrich provides the C and n values and $r(K)$ is calculated from

$$r(K) = \frac{(\mu/\rho)_{\max}^{K \text{ edge}}}{(\mu/\rho)_{\min}^{K \text{ edge}}} = \frac{C_K \lambda_K^{n_K}}{C_{KL} \lambda_{KL}^{n_{KL}}}$$

$$= \frac{C_K}{C_{KL}} \lambda_K (n_K - n_{KL}) \quad (26)$$

where λ_K is the wavelength at the absorption edge. The $r(K)$ and total $r(L)$ values in Fig. 52 were calculated from Heinrich's C and n data, Eq 26, and the expression

$$r(L) = \frac{C_{KL}}{C_{LM}} (\lambda_{L_3 \text{ edge}})^{n_{KL} - 2.6}$$

Reed [118] has used the approximation $r(L) = 4$ and $r(K) = 8.3$, since the fluorescence of the K lines for $Z < 20$ and the L lines for $Z < 50$ is usually negligible. Heinrich and Yakowitz [349] have shown that the error introduced by a 10 percent error in r is negligible.

The fluorescence yield values for the exciting radiation can be calculated from the expression proposed by Burhop [354]:

$$\left(\frac{\omega}{1 - \omega} \right)^{1/4} = A + BZ + CZ^3 \quad (27)$$

Colby [45] fitted this expression to some of the data of Fink [352] and obtained the values of the coefficients for K, L, and M fluorescence yields. The values for ω

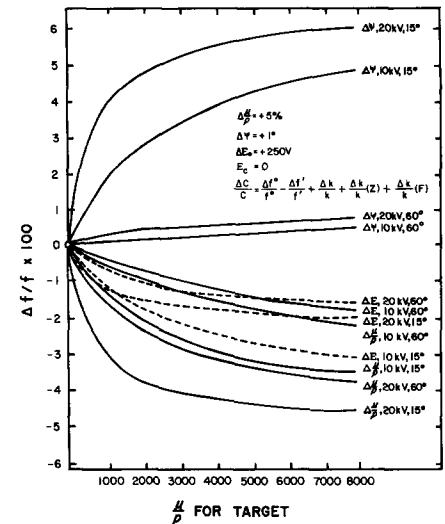


Fig. 51—The error in the absorption correction factor, $\Delta f/f$, as a function of the target mass absorption coefficient. $\Delta f/f \approx \Delta C/C$ in the absence of atomic number and characteristic fluorescence effects if there is no error in the measurement of k . Errors are plotted for 10 and 20 kV and for $\psi = 15$ and 60 deg for each of three possible uncertainties: (1) $\Delta(\mu/\rho) = 5$ percent, (2) $\Delta\psi = 1$ deg, and (3) $\Delta E_0 = 250$ V. At 10 kV with a take-off angle of 15 deg, a 5 percent error in μ/ρ results in a $\Delta f/f$ value of 3% when the M/e ratio of the target is ~ 4500 cm²/g. Curves from Heinrich and Yakowitz [346].

calculated using the Colby coefficients and Eq 27 are plotted in Fig. 52. Reed [118] uses the Wentzel [353] formula where $\omega = Z^4/a + Z^4$ with $a = 10^6$ for $\omega(K)$ and $a = 10^8$ for $\omega(L)$. The two expressions for $\omega(K)$ differ by less than 3 percent for Z from 28 to 50 and by less than 4 percent for Z from 14 to 27; however, the difference is considerably larger for $r(L)$, increasing from 14 percent at $Z = 90$ to 25 percent at $Z = 50$. Martin and Poole [278] reported a best fit curve to the data of Fink et al [352], developed by Bambynek et al [351], and they recommend it as the most reliable source of $\omega(K)$ values available today.

Heinrich and Yakowitz [349] did find

Table 22—Relative Error in the $f(\chi)$ for Al in a 50-50 Al-Mg Alloy (from Yakowitz and Heinrich, Ref. 347)

Acceleration potential (kV)		5		10		15	
Take-off angle (°)		15	60	15	60	15	60
Parameter in error	Magnitude of error	Relative Error=100Δf(χ)/f(χ)					
$\Delta(\mu/\rho)/(\mu/\rho)$	9.3%	4	2	7	3	9	5
ΔE_0	250 volts	3	1	3	1	3	1
$\Delta\psi$	0.5°	1	0	2	0	3	0
Most probable total error		5	2	8	3	10	5

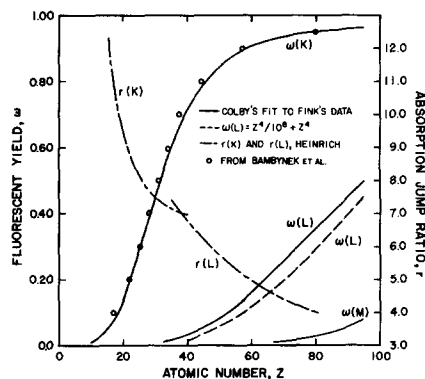


Fig. 52—On the left-hand axis, the K, L, and M fluorescent yields, ω , are plotted as a function of atomic number. On the right-hand axis, the K and L absorption jump ratios, r , are plotted as a function of atomic number. The ω curves are from J. Colby's [45] fit to the data of Fink et al [352]. Selected points from the Bambynek et al [351] curve for $\omega(K)$ are plotted as closed circles. A $\omega(L)$ curve is also plotted for the Wenzel [353] formula, where $\omega(L) = Z^4/(10^4 + Z^4)$. The r values are from Heinrich [350].

significant error in the characteristic fluorescence correction as a result of uncertainty in ω . In a 10Fe-Ni alloy, relative errors of about 5 percent accompanied a 20 percent error in ω (ΔC (absolute) ranged from 0.3 to 0.5 percent Fe). They also found the primary source of error in the fluorescence correction to be in the correction model and in ω . The calculated concentrations from the Reed [118] and Castaing [4] models differed significantly; in 10 percent Fe alloy ($C_{\text{Reed}} - C_{\text{Castaing}}$) = 1 percent for a 10 percent relative error at 15 kV.

When characteristic fluorescence is the predominant correction, several authors [126, 328, 344, 355, 356] have reported results that are not usually as good as when an absorption correction of similar magnitude predominates. This is presumably due to error propagation (absorption effects are usually present) and inadequacies in the fluorescence correction model. Because fluorescence effects are restricted to a reduced range of atomic numbers, data covering a wide range of real alloy systems are not nearly as abundant as for the absorption correction.

Atomic Number Correction/ Next let us consider what is perhaps the most interesting of the corrections, the atomic number correction, where widespread use is being made of the expression proposed by Duncumb and Reed. An analytic expression for $k_g(C_A F(0)/F(0)^0)$ is needed in order to replace the numerical integration in Eq 13. Introducing the following definitions:

dn_K = number of K ionizations produced per unit path length dx .
 $Q_K(E)$ = K ionization cross section of A atoms for electrons; a function of the energy E of the electron.

$\rho^0 N_0/A$ = number of A atoms per unit volume, where ρ^0 is the density of the pure material, N_0 is Avagadro's number, and A is the atomic weight of element A.
 n_K = total number of K ionizations produced per incident electron.

Then, by definition,

$$dn_K \equiv Q_K(E) N_0 d(\rho x)^0 / A$$

The path length of interest is from the point of impingement to the point where the mean electron energy becomes E_c , since for $E < E_c$ no further ionization can take place. Since at $x = 0$ $E = E_0$, changing variables yields

$$n_K = \frac{N_0}{A} \int_{E_0}^{E_c} \frac{Q_K(E) dE}{dE/d(\rho x)^0} \quad (28)$$

The number of ionization events must be converted to the actual X-ray photon intensity. A single ionization can produce (through the decay of excited states) either a K photon or ejected electron (radiationless transition = Auger effect). The fluorescence yield, ω , is the ratio of the number of X-ray photons to the number of ionizations.

Because the total number of K photons is made up of $K\alpha_1$, $K\alpha_2$, and $K\beta$ radiation, to arrive at the intensity of $K\alpha_1$ X-radiation the total X-ray intensity generated must be multiplied by a factor $G = \#K\alpha_1 / (\#K\alpha_1 + \#K\alpha_2 + K\beta)$, where the # refers to the number of photons of each type of radiation. The generated intensity (neglecting backscatter) then is given by

$$I_g^0 = \omega_K(A) G \frac{N_0}{A} \int_{E_0}^{E_c} \frac{Q_K(E) dE}{dE/d(\rho x)^0} \quad (29)$$

It is necessary to take into account the loss

of ionization due to the backscattering of those electrons with energies in excess of E_c .

Call η the fractional loss of incident electrons, or simply the ratio of the number of electrons backscattered to the number of incident electrons. To calculate the X-ray intensity we need to know not the number of electrons lost but the useful ionization energy lost; thus, we define R as the backscatter coefficient representing the fraction of the total possible ionization (if all electrons remained in the target) that actually occurs. Then $1 - R$ is the fraction of the total ionization that is lost through backscatter and would be given by η if all the electrons were backscattered without energy loss ($E = E_0$). Its value is generally calculated from experimental data describing the energy distribution of backscattered electrons, $d\eta/dW$ versus W , where $W = E/E_0$. The intensity that could have been generated by the backscattered electrons is obtained by integrating Eq 29 over the interval E to E_c (WE_0 to E_c). To obtain the total lost intensity, one must integrate over all the backscattered electrons from $W_c = E_c/E_0$ to $W = 1$, that is, from E_c to E_0 . The fractional loss of generated intensity is then given by

$$1 - R = \frac{\int_{W_c}^1 \frac{d\eta}{dW} \int_{E_c}^{E_0} \frac{Q_K(E) dE}{dE/d(\rho x)} dW}{\int_{E_0}^{E_c} \frac{Q_K(E) dE}{dE/d(\rho x)}} \quad (30)$$

Substituting the stopping power, S , for $-dE/d(\rho x)$ gives

$$R = 1 - \frac{\int_{W_c}^1 \frac{d\eta}{dW} \int_{E_c}^{W E_0} \frac{Q_K(E) dE}{S} dW}{\int_{E_0}^{E_c} \frac{Q_K(E) dE}{S}} \quad (31)$$

Table 23—The Backscatter Coefficient, R , as a function of z and $1/U$ (from Duncumb and Reed, Ref. 115)

1/U	0.01	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
z											
0.	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
10.	0.934	0.944	0.953	0.961	0.968	0.975	0.981	0.988	0.993	0.997	1.000
20.	0.856	0.873	0.888	0.903	0.917	0.933	0.948	0.963	0.977	0.990	1.000
30.	0.786	0.808	0.828	0.847	0.867	0.888	0.911	0.935	0.959	0.981	1.000
40.	0.735	0.760	0.782	0.804	0.827	0.851	0.878	0.907	0.938	0.970	1.000
50.	0.693	0.718	0.741	0.764	0.789	0.817	0.847	0.881	0.919	0.959	1.000
60.	0.662	0.688	0.713	0.737	0.764	0.793	0.825	0.862	0.904	0.950	1.000
70.	0.635	0.663	0.687	0.713	0.740	0.770	0.805	0.844	0.889	0.941	1.000
80.	0.611	0.639	0.665	0.691	0.718	0.750	0.785	0.826	0.874	0.932	1.000
90.	0.592	0.613	0.639	0.665	0.695	0.730	0.767	0.811	0.862	0.924	1.000
99.	0.578	0.606	0.634	0.661	0.691	0.725	0.763	0.806	0.858	0.921	1.000

1) $1/U = E_c/E_0$; 2) z = atomic number

Duncumb and Reed [115] have used the experimental data of Bishop [357,358] ($d\eta/dW$ versus W) and calculated R values by (1) using the Bethe expression for S , (2) letting $J = 11.5Z$, and (3) using the Webster expression [359]

$$Q_K(E) = \frac{C}{E^2} \frac{\ln U}{U^m} \quad (32)$$

with $m \simeq 0.8$ and $U = E/E_c$. Heinrich and Yakowitz [260] have shown that any uncertainty in the Q used in the calculation of R has a negligible effect on the atomic number correction. The values for R from Duncumb and Reed [115] are given in Table 23 as a function of Z and $1/U$. Duncumb [361] has derived a 36-term polynomial which gives an excellent fit to these values obtained by full integration. The polynomial will provide R for any Z and any W . This polynomial is as follows:

$$\begin{aligned} R - 1 = & + (-0.581 + 2.162W - 5.137W^2 + 9.213W^3 - 8.619W^4 \\ & + 2.962W^5) \times 10^{-2} \times Z \\ & + (-1.609 - 8.298W + 28.791W^2 - 47.744W^3 \\ & + 46.540W^4 - 17.676W^5) \times 10^{-4} \times Z^2 \\ & + (5.400 + 19.184W - 75.733W^2 + 120.050W^3 - 110.700W^4 \\ & + 41.792W^5) \times 10^{-6} \times Z^3 \\ & + (-5.725 - 21.645W + 88.128W^2 - 136.060W^3 \\ & + 117.750W^4 - 42.445W^5) \times 10^{-8} \times Z^4 \\ & + (2.095 + 8.947W - 36.510W^2 + 55.694W^3 - 46.079W^4 \\ & + 15.851W^5) \times 10^{-10} \times Z^5 \end{aligned}$$

The agreement between the direct experimental measurements of R by Derian [362,363] and the Duncumb data is good. Heinrich and Yakowitz [360] have discussed the significant variations in published R data. Figure 53, from Heinrich and Yakowitz [360], shows the effect of the combined uncertainty in R and J in a 50Al-50Au alloy as a function of potential.

The generated intensity can now be written as

$$I_g^0 = \omega_K(A)G \frac{N_0}{A} R^0(A) \int_{E_c}^{E_0} \frac{Q_K(E) dE}{S} \quad (33)$$

To convert this to the actual measured intensity one simply multiplies by $f(x)$ (the emitted fraction) and the included solid angle $\Omega/4\pi$. Thus, the number of emitted photons per incident electron, I , is

$$I = \omega_K(A)G \frac{N_0}{A} R^0(A) f(x)^0 \frac{\Omega}{4\pi} \int_{E_c}^{E_0} \frac{Q_K(E) dE}{S} \quad (34)$$

The product of I , the beam current, and a factor which accounts for the spectrometer efficiency would provide the absolute photon intensity in photons per second. The next problem is one of attaining a value for the integral in Eq 33. Because $k_g = C_A F(0)' / F(0)^0 = I_g' / I_g^0$ and the number of A atoms per unit volume in an alloy is $C_A \rho N_0 / A$, the ratio k_g can be written

$$k_g = \frac{I_g'}{I_g^0} = \frac{C_A R' \int_{E_c}^{E_0} \frac{Q_K(E) dE}{S'}}{R^0 \int_{E_c}^{E_0} \frac{Q_K(E) dE}{S^0}} = C_A \frac{F(0)'}{F(0)^0} \quad (35)$$

In taking the ratio $\omega_K(A)$, G , N_0 , and A cancel out. Duncumb and Reed [115] as-

$$\frac{dE}{d(\rho X)} = S = \text{constant} \frac{1}{E} \frac{Z}{A} \ln \frac{1.166E}{J} \quad (37)$$

To calculate S' and R' the general practice has been to use weight concentration averages;

$$S' = \sum C_i S_i, R' = \sum C_i R_i, \eta' = \sum C_i \eta_i \quad (38)$$

Since Duncumb and Reed [115] evaluate S' at a mean energy $E = (E_0 + E_c(A))/2$, the constant and $1/E$ in Eq 37 disappear in forming the ratio S^0/S' .

In the calculation of the concentration of element A, the excitation potential of element A, $E_c(A)$, should be used in obtaining the values of $S_A, S_B, \dots, S_N$ which are used to calculate S_A' . We have encountered several cases where investigators have used $E_c(B), \dots, E_c(N)$ in calculating $S_B, \dots, S_N$; they assume that the S_N values depend only on the characteristics of element N and E_0 . This neglects the fact that the quantity of interest is the stopping power of element N for electrons that have sufficient energy to excite element A, independent of the excitation potential of element N. The same is true for the backscatter correction, R_A' ; a loss of ionization only occurs when $E > E_c(A)$. Recall that in evaluating the integral $\int (Q/S) dE$, the energy range of interest is E_0 to $E_c(A)$.

J , the mean ionization potential, is of considerable importance and a variety of expressions have been proposed and used: $J = 11.5Z$, based on Bloch [365]; $J = 12.4Z + 0.027Z^2$, Caldwell [366]; $J = 9(Z + Z^{1/3})$, Springer [367]; and $J = 9.76Z + 58.5Z^{-0.19}$, Berger and Seltzer [368]. Duncumb et al [120] obtained the following expression for J , which provided the best results in a group of concentrations calculated from measured k values:

$$\frac{J}{Z} = 14(1 - e^{-0.12Z}) + \frac{75.5}{Z^2/7.5} - (Z/(100 + Z)) \quad (39)$$

Heinrich and Yakowitz [360] have published a curve of J versus Z comparing all of the J expressions except Springer's. Duncumb and Reed's [115] J values are shown in Table 24. Heinrich and Yakowitz [360] have shown that substantial differences in calculated k values can be introduced by the use of different J values, for example, k (Duncumb and Reed) $\simeq 1.1$ (Bergen and Seltzer) in a 20Al-80Ag alloy. Most investigators presently prefer the Duncumb [115, 120] J values even though they are empirical.

Sufficient data are now available (R, J, τ, ω) to determine, for a given set of experimental conditions (E_0 and ψ), the concentration C_A from a measured k_A in the ab-

sume that S^0/S' varies slowly with energy and, thus, can be evaluated at a mean energy taken to be $(E_0 + E_c)/2$, as proposed earlier by Thomas [364]. The energy loss is a function of Z and E . Assuming that these variables are separable, that is, $dE/d(\rho x) = S(Z)f(E)$, it is possible to write

$$k_g = \frac{C_A R' \int_{E_c}^{E_0} \frac{Q_K(E) dE}{S'(z)f(E)}}{R^0 \int_{E_c}^{E_0} \frac{Q_K(E) dE}{S'(z)f(E)}} = C_A \frac{R' S^0}{R^0 S'} \quad (36)$$

where, from Eq 35,

$$\frac{R'/S'}{R^0/S^0} = \frac{F(0)'}{F(0)^0}$$

The most frequently used energy loss expression is that of Bethe [41]:

$$\frac{dE}{dX} = \frac{-2\pi e^4}{E} \frac{\rho N_0}{A} z \ln \left[\left(\frac{e}{2} \right)^{1/2} \frac{E}{J} \right]$$

or

sence of continuum fluorescence effects. To make that correction, use h from $1.2A/Z^2$, σ from Eq 22, $f(\chi)^0$ from Eq 23, $f(\chi)'$ from Eq 24, R^0 from Table 23, S^0 from Eq 37 and Table 24, S' and R' from Eq 38, r and ω from Fig 52, (μ/ρ) from Ref 350, and γ from Eq 25. A complete hand calculation is carried out in detail in Appendix 2, and the output from a computer program for the same system is also illustrated.

Philibert and Tixier [369] have recently devised a method for evaluating the integral in Eq 35 without making the simplifying assumptions required to avoid the

integration. They have evaluated $\int_{E_0}^{E_c}$

$Q_K(E) dE/(dE/d(\rho X))$ for both pure and complex targets. They use the following expressions for Q and $dE/d(\rho X)$, Bethe [41] and Bethe, Rose, and Smith [370], and then integrate in terms of a logarithmic integral function:

$$Q_K(E) = \frac{\pi e^4 Z_i b_i \ln U}{E_c^2 U} \quad (40)$$

$$\frac{dE}{d(\rho X)} = \frac{-2\pi e^4 N_0}{UE_c} \sum C_A \frac{Z(A)}{A} \ln \frac{1.166 UE_c}{J(A)} \quad (41)$$

U is E/E_c , Z_i is the number of electrons in the excited shell, and $b_i = 0.35$ for the K shell and 0.25 for the L shell. Evaluation of the integral then provides values for I_g (Eq 29). This procedure avoids the earlier assumptions made to avoid the integration and should improve the atomic number correction.

Duncumb, in a review presented at the Fifth National Conference, recommended the use of the full integration procedure [371]. The Philibert-Tixier [369] procedure is, at present, included in only three of the 40 available computer programs, namely, those by Philibert and Tixier [369], Colby

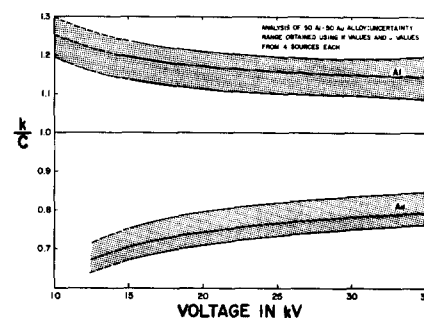


Fig. 53—The uncertainty in calculated k/c ratios in a 50Al-50Au alloy as a function of the acceleration potential. The bands are due to variations in R and J values. At 20 kV uncertainties in J and R can lead to calculated k values (in this alloy) ranging from 56 to 61 percent Al and from 36 to 40 percent Au. Curves from Heinrich and Yawowitz [360].

Table 24—The Mean Ionization Potential, J , as a Function of Atomic Number (from Duncumb and Reed, Ref. 115)

z	$J(eV)$	z	$J(eV)$	z	$J(eV)$	z	$J(eV)$
6	146	29	377	52	706	75	1017
7	135	30	392	53	720	76	1031
8	127	31	407	54	734	77	1044
9	123	32	422	55	747	78	1057
10	123	33	437	56	761	79	1071
11	126	34	451	57	775	80	1084
12	133	35	466	58	788	81	1097
13	142	36	481	59	802	82	1111
14	154	37	495	60	815	83	1124
15	166	38	510	61	829	84	1137
16	180	39	524	62	843	85	1151
17	194	40	538	63	856	86	1164
18	209	41	553	64	870	87	1177
19	224	42	567	65	883	88	1191
20	239	43	581	66	897	89	1204
21	255	44	595	67	910	90	1217
22	270	45	609	68	923	91	1231
23	286	46	623	69	937	92	1244
24	301	47	637	70	950	93	1257
25	316	48	651	71	964	94	1270
26	332	49	665	72	977		
27	347	50	679	73	991		
28	362	51	692	74	1004		

[45], and Beaman [126]. Walitsky and Colby [373], using the Berger-Seltzer expression, found that the Philibert-Tixier procedure gave better results than the Duncumb-Reed procedure in the analysis of Cu in three Cu-Au alloys. In the systems studied by Beaman [126], the Philibert-Tixier procedure did not provide results as good as those of Duncumb and Reed; however, it gave better results than those of Thomas [364]. Note, however, that Philibert and Tixier use $J = 11.5Z$. Poole [374] reported good results with the Thomas [364] procedure.

Continuum Fluorescence Correction/ The continuum fluorescence correction is generally the smallest correction and in the past has usually been neglected in the presence of the other larger corrections. The most comprehensive approach to the problem has been presented by Henoc [119] who, in his thesis [375] written in 1962, derived an expression for the contribution to the emergent intensity, I_{cf} , arising as a result of excitation by the continuous spectrum. The expression is lengthy because of the need to sum the contribution due to the continuum over the interval from λ_{SWL} to λ (edge of the analyzed element). Henoc uses Kramers' [376] expression for the intensity of the continuum radiation as a function of λ where $I_\lambda = KZ(1/\lambda_{SWL} - 1/\lambda)/\lambda$. K , the Kramers constant, is a source of error in the calculation.

In Eq 19, k_1 ($k_1 = I_{cf}'/I_{cf}^0$) is calculated from Henoc's expression for I_{cf} . Henoc [377] calculates I_g^0 in a manner similar to that of Philibert and Tixier. I_p^0 follows from I_g^0 since $I_p^0 = I_g^0 R^0 f(\chi)^0$. k_2 is calculated from $k_2 = I_{cf}^0/(I_p^0 + I_{cf}^0)$. Figure 54, from Henoc's [119] work shows the fraction of the total emitted intensity due to continuum fluorescence (I_{cf}^0/I_t^0) and compares some of the theoretical values of Henoc with a few experimental values.

Springer [378] has developed an expression for I_{cf}/I_p which can be used to perform the continuum fluorescence correction. Here

$$k_e = \frac{I_p'}{I_p^0} = k \frac{I_t^0}{I_t'} \frac{I_p'}{I_p^0} = k \frac{I_t^0/I_p^0}{I_t'/I_p'} \quad (42)$$

$$= k \frac{(I_p^0 + I_{cf}^0)/I_p^0}{(I_p' + I_{cf}')/I_p'} = k \frac{(1 + I_{cf}^0/I_p^0)}{(1 + I_{cf}'/I_p')} \quad (42)$$

For K radiation Springer has found

$$\frac{I_{cf}}{I_p} = 4.34(10^{-6}) \frac{r_K(A) - 1}{r_K(A)} \quad (43)$$

$$\bar{Z} A E_c(A) \frac{\mu_A^{\max}}{\mu_{\text{alloy}}^{\max}} H(g, U_0)$$

where

$\mu_A^{\max}$ = maximum (μ/ρ) value of element A for radiation with $\lambda = \lambda(\text{edge}, A)$,

$\mu_{\text{alloy}}^{\max}$ = same, except of alloy,

$\bar{Z}$ = mean atomic number of alloy,

$U_0 = E_0/E_c(A)$,

$g = \frac{(\mu/\rho)_A^{\text{K}\alpha}}{(\mu/\rho)_{\text{alloy}}^{\text{K}\alpha}} (\csc \psi)$, and

$H(g, U_0) = \frac{\ln(1 + gU_0)}{gU_0}$, evaluated for each range between the absorption edges in the interval E_0 to $E_c(A)$.

Springer and Rosner [379] point out that the random application of the continuum fluorescence correction to a series of alloys provides little insight into the correction factor, because in the great majority of cases the correction is less than ± 1 percent which is within experimental error. When they applied the correction to 17 specimens whose continuum fluorescence correction exceeded 1 percent, they found

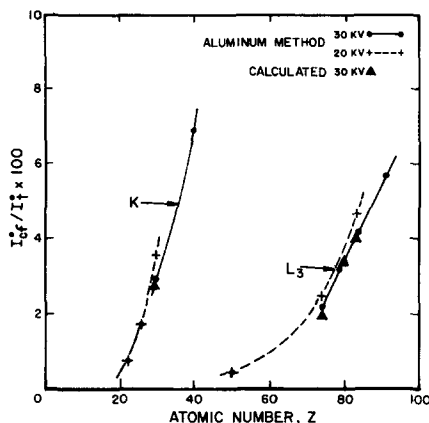


Fig. 54—The ratio of indirect to direct X-ray production as a function of atomic number. I_{cf} is the emitted intensity occurring due to excitation by continuous fluorescence radiation and I_t^0 is the total emitted intensity. Curves from Henoc [119].

Table 25—The Magnitude of the Continuum Fluorescence Correction in a 40% Cu–60% Au Alloy¹

Alloy concentration Investigator	40% Cu		60% Au	
	Beaman	Springer ²	Beaman	Springer ²
Method of obtaining k/C	k/C values			
Experimental	1.05 ₂	1.03 ₅ ³	0.85	0.85 ₄ ³
Calculated without continuous fluorescence	1.06 ₆	1.00	0.84 ₆	0.85 ₂
Calculated with continuous fluorescence	1.07 ₀	1.02	0.83 ₇	0.83 ₄
Calculated without continuous or characteristic fluorescence ⁴	1.02			

1) 25 kV, $\psi=15-18^\circ$; 2) Ref. 379; 3) interpolated; 4) $\text{CuK}\alpha_1$ fluoresced by $\text{AuL}\alpha$

a small overcorrection. A histogram of $C_{\text{corrected}}/C_{\text{true}}$ versus frequency peaked at 101.5 with the continuum fluorescence correction and at 99.5 without the continuum fluorescence correction. Hence, they suggested that the normal procedure of neglecting the correction might be advisable.

Our results on a 40Cu-60Au alloy are not in complete accord with those of Springer and Rosner, as shown in Table 25. Our corrections were made using the Duncumb and Reed atomic number correction, the Heinrich modification of the Duncumb and Shields absorption correction, Reed's characteristic fluorescence correction, and Henoc's [377] program for the continuum fluorescence correction. In the Cu-Au alloy, the magnitude of the correction based on the Henoc program is less than half of that extracted from the results of Springer [379], and it was not possible to ascertain whether or not Springer corrected for the excitation of $\text{CuK}\alpha_1$ by $\text{AuL}\alpha$ in the Cu computations.

Myklebust, Yakowitz, and Heinrich [380] have recently tried to establish guidelines that would enable an investigator to know when the continuum fluorescence correction would be significant. Such effort is certainly justified because, as they point out, in a computerized correction scheme about 50 percent of the computation time is spent on the continuum fluorescence correction. Hence, it is expensive to perform, and it would be useful to know under what conditions it could be safely neglected. They calculated the probe ratio for a true concentration of 10 percent in 48 binary alloys with and without the continuum fluorescence correction and calculated H , the relative difference between the two, that is, $H = \{k(\text{with cf}) - k(\text{without cf})\}/k(\text{without cf})$. They sought the conditions that would yield $H < 1$ percent and render the correction negligible. They concluded that it could

be neglected when (1) $f(\chi') < 0.9$, (2) $C(A) > 0.5$, (3) $\chi' > 300$; or (4) using K lines for $Z(A) < 20$ and L lines for $Z(A) < 50$. Some of the reasons for these apparent boundaries are clear; Fig. 54 indicates that the production of continuum radiation is negligible below the Z values stated in four above conditions. When the generation of continuum radiation is significant, it introduces a problem if it can escape from the target (low absorption, high $f(\chi)$, and low χ'), for example, with a hard line in a soft matrix, as might be encountered in biological materials.

In Fig. 55 we have used the Henoc program to compute the relative error in the calculated k caused by neglecting the continuum fluorescence correction as a function of concentration, potential, and ψ in the CuAu system. The Cu, but not the Au (L line), is sensitive to potential and ψ and the χ' criterion of Myklebust et al [380] appears to be valid in this system. We found, however, a more significant dependence on potential than Myklebust et al [380] did, who found the correction to be independent of potential between 15 and 35 kV. The relative error for Cu nearly doubles as the potential decreases from 25 to 15 kV and more than doubles as ψ increases from 18 to 75 deg. Springer [379] found a severe correction in the PtAs_2 system (As K at 25 kV and $\psi = 75 \text{ deg}$) where $\chi' = 510$. Thus, studying particular systems and extrapolating to cover all systems and conditions can be risky. What would be desirable is a simple approximation based on the Henoc procedure [119] that would serve as an indicator for further complete calculations.

We can summarize the findings of others as follows: Springer [378] has found the correction to be generally small, usually less than 1 percent of the measured intensity ratio, and concludes that neglecting it is often, but not always, justified.

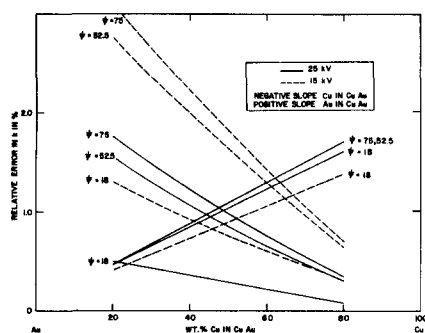


Fig. 55—The relative error in calculated intensity ratios caused by neglect of the continuous fluorescence correction in the Cu-Au alloy system plotted as a function of weight percent Cu. The curves with negative and positive slopes are for $k(\text{Cu})$ and $k(\text{Au})$ respectively. The errors are calculated for $\psi = 75, 52.5$, and 18° at 15 and 25 kV. χ^* values for 40 percent Cu in the Cu-Au alloy are 151, 187, and 475 for $\psi = 75, 52.5$, and 18° , respectively.

Springer and Rosner [379] have reported significant improvements in some computed concentrations when applying the Springer [378] continuum fluorescence correction, but found the correction negligibly small in most cases. Brown et al [381], in their TEP work, have reported a significant improvement in some of their results when a correction was applied. In limited experience with the Henoc program, we have not encountered a correction greater than 0.5 weight percent. Kirianenko et al [382] have reported absolute corrections of less than 0.4 percent in several U alloys. Henoc et al [50] have illustrated remarkable and significant effects at phase boundaries. Brown [383] has found the correction negligible for K lines if $Z < 20$, for L lines if $Z < 50$ (71), or for $\lambda > 2.1 \text{ \AA}$. Myklebust et al [380] found H values in excess of 2 percent (at 25 kV, and $C = 10$ percent) for Zn $K\alpha$ in B and P; Zr $K\alpha$ in B, P, Zn, Rh, and Ne; Yb $L\alpha$ in B and Zn; and Hg $L\alpha$ in B and P.

The evidence appears to be sufficient to justify having the correction at least approximated in any computer program, and any correction program written in the future should include the correction since improvements in experimental results and other phases of the correction will increase the significance of this effect.

Computer Programs to Convert k to C / Computer programs are needed in the conversion of electron probe X-ray intensity ratios, k , to chemical compositions, C , primarily because some of the correction parameters are functions of concentration and, hence, make successive approximations necessary. This iteration procedure is illustrated in Appendix 2. While the analytical expressions just discussed are not complex, a total correction formula is

lengthy and iteration in multicomponent systems makes hand calculations formidable. Just the existence of 40 programs, by authors from Canada, England, France, Germany, Italy, Japan, Sweden, and the U.S., attests to the need for a good correction program.

In a recent investigation by Beaman and Isasi [202], all of the published and many of the unpublished computer programs used in quantitative electron probe analysis were examined and critically evaluated with the following objectives: (1) to list in one location the features and capabilities of all available programs, (2) to critically examine each program with respect to its accuracy, content, and versatility; and (3) to establish what a program should and should not contain in an attempt to diminish duplication and the proliferation of inadequate programs. Fulfillment of the first two objectives should allow each analyst to select the program most suitable for his needs, based upon the type of problem he normally encounters, the computer facilities at his disposal, his interest in evaluating correction procedures, etc. The validity of the third objective is supported by an extrapolation of a plot of the number of programs available as a function of time, which indicates that, at our present production rate, at least 150 programs should be available by 1975. Programs by Mason, Frost, and Reed [308], Duncumb and Jones [127], Shaw [384] and Colby [45] were found to be outstanding. The last was recommended for use in metallurgical applications and the others for use in both metallurgical and geological applications. Several other programs were found to have specific areas of usefulness and the reader is referred to Ref 202 for details.

Because many fine programs are available and are easy to use, on a routine basis, for performing quantitative corrections in metallurgical and geological systems, Beaman and Isasi [202] recommended that before an analyst decides to write his own program he should seriously consider using one of these published programs. Unless, of course, he plans on eliminating many of the existing deficiencies. The addition of another incomplete program to the copious list of existing programs would certainly be of limited value.

Monte Carlo and Transport Equation Techniques/ There is more than one approach to the problem of quantitative analysis, and to this point the discussion has been restricted to the classical, or ZAF, approach in which a physical model is required to develop an analytical expression for each of the correction phenomena. As has been shown, these models provide good results and errors are, for the most part, due to uncertainties in the physical constants utilized (μ/ρ , r , ω , J , R , etc.).

However, it was the failure of the $\bar{Z}AF$ approach to provide accurate quantitative results in all materials, particularly at low Z under a variety of operating conditions, that led to the use of the transport equation program (TEP) [385] and Monte Carlo (MC) [132, 386, 387] techniques. In the MC technique a number of individual electron trajectories are generated in a computer, where it is assumed that the electron travels in small, straight line segments between random scattering events (elastic and inelastic). In the TEP a total beam of electrons undergoes continued scattering as it penetrates the target, the extent of which is predicted by a Boltzman transport equation.

MC and TEP calculations which have heretofore been confined to the realm of theory have just recently been incorporated into computer programs for use in quantitative analysis by Pascal (MC) [388] and Brown (TEP) [389]. Both approaches require detailed fundamental information concerning the interaction of primary electrons with the atomic nucleus (elastic scattering) and atomic electrons (inelastic scattering). Theoretical expressions are required for electron scattering, energy loss, and the ionization cross section. This condition for good fundamental data is rewarded by extremely useful output: the distribution in energy and depth of primary electrons, $\phi(\rho z)$, $f(\chi)$, distribution in energy of backscattered electrons, range, etc.

Ogilvie and Brown [390] have demonstrated the use of TEP in obtaining "limiting $f(\chi)$ curves" for A in A and a trace of A in B, that is, the two curves necessary for analyzing A in an A-B alloy. It is now apparent that the results from MC and TEP calculations are about as good as the existing experimental data. Brown, Wittry, and Kyser [381] have compared TEP results and Bishop [386] and Brown [391] MC results with experiment. Brown [391] and Brown et al [348, 381, 385] have demonstrated the use of TEP in making practical corrections, while Bishop [386] has done the same with MC results. Pascal [388] has shown that MC techniques can be successfully and economically incorporated into a programmed correction scheme; in his program, if the intensities for the standards have been previously calculated and stored, $10(n + 1)$ seconds are required to carry out the calculations in an n -component system. A program based on the use of TEP written by Brown [389] has just become available.

It is safe to assume, in view of this past work, that the use and success of MC and TEP techniques will increase as more and accurate fundamental data become available. While these computer methods of direct calculation are expensive at the

Table 26—Historical Summary of the Qualitative Analysis Capability of the Electron Probe Analyzer

Principal author	Ref. No.	Year work done	Predominant correction	No. of analyses	Comment	% of analyses within						estimate that 67% of analyses within ± %
Poole	397	1964	Z, A	150	uncorrected: corrected using Thomas correction:	±0.5%	±1.5	±2.5	±3.5	±4.5	±5.5	4.5
Belk	398	1965	Z, A	10	Cu-Ni-Sn alloy studied by Birmingham Users Group:							5-10
Belk	333	1965	Z, A	128	Belk correction scheme applied to Poole and Thomas data:	20	42	60	70	77		3-2
Colby	356	1965	A	5	analyses of Fe in Fe-Cr at 20 kV; C<11%; DS* correction:	0	20	40	60	60		3
			F	5	analyses of Cr in Fe-Cr at 20 kV; C<11%; Castaing correction:	0	0	0	20	20		6
Birks	355	1966	Z, A, F	7	Washington Users Group round robin samples; no correction in Cu-Zn; A and F in Fe-Ni; A and Z in FeS ₂ :	for concentration = 10-20% >20% no correction applied 5 2-3 3 5 2-3 5-8 2-3						
Poole	374	1967	Z, A	229	use Poole and Thomas data; DS for A and DR for Z:	17	39	55	62	66		4.5
Duncumb	115	1967	Z, A	48	alloys used to obtain J/Z giving best fit to expt. data; F and A correction <2%:	15	42	58	66	72		3.5
Beaman	344	1967	Z, A, F	52	technique evaluation; best techniques gave following results: Z, A in the z interval of 22-33, small corrections: A in Al-Mg alloys, large corrections: Z predominates: F predominates:							1-2 3-4 4-6 3-5
Heinrich	116	1968	Z, A, F	109	selected alloys from Poole and Thomas data; omitted inconsistent data, f(X)<0.6, k<0.5; used H, Reed with P _{ik} =2.4 and modified Poole and Thomas Z correction:	16	51	75	86	94		2.2
Duncumb	120	1968	Z, A	101	alloys with large Z correction; H for A, DR for Z:	43	72	86	92	96		1.4
Duncumb	120	1968	Z, A, F	333 121	binaries; Poole and Thomas data; H+DR+Reed correction: silicates; H+DR+Reed correction:	19	45	59	73	78		3
Beaman	328	1968	Z, A, F		Midwest Users Group; concentration 10-80%; well characterized FeNi, CuZn, TiNb and CrCoMo; DS+DR+Reed correction:	29	79	93	99			1.3
Beaman	126	1969	Z, A	39	alloys with a predominant Z correction; H+DR correction:	21	67	95	98	100		1.5
			Z			13	51	64	85	95		2.5
			Z, A	22	alloys with a small but predominant A correction; H+DR: DS+DR correction:	32	68	96	100			1.5
			A		AW+DR correction:	32	64	86	100			1.5
			A		Tong correction:	14	64	82	96			1.5
			A	11	Al in AlMg alloys with a large A correction; Tong correction:	36	59	82	91	100		1.7
			A			18	45	63	72	81		3.0
French	399	1969	Z, A	8	analyzed Al in Fe+0.85% Al alloy; 8 instruments at 10kV with ψ=17 to 18°; DS or Philibert or H for A; R/S type correction for Z:	k=0.47±.04% C=0.92±.10%						<1%
Poole	51	1970			expected accuracy in EPA							1

*Symbols have the following meaning: DS=Duncumb & Shields; DR=Duncumb & Reed; H=Heinrich; PT=Philibert & Tixier; AW=Andersen & Wittry.

present time, it is probable that they will ultimately be used in general correction programs. It is certain that MC and TEP calculations will provide information that will permit improvement in the classical expressions. Hopefully, information will be forthcoming in the range of low Z , where the classical expressions have often provided dismal results.

The Empirical Approach of Ziebold and Ogilvie/ The last approach to quantitative analysis that we will discuss is the empirical solution suggested by Ziebold and Ogilvie [123] in 1964. They proposed that for an A-B binary alloy, $C_A/k_A = \alpha_A + (1 - \alpha_A)C_A$ (recall Eq 5), which indicates that a plot of C/k versus C will be linear with an intercept of α and a slope of $(1 - \alpha)$. In multicomponent systems, α is given by Eq 6 and there is an α and an Eq 5 for each component in the system. Lachance [392] has written a computer program to solve a group of j ($j = 3$ to 10) simultaneous equations each involving k , C , and α . Depending on what is known, these may be solved for C , k , or α . Generally, k is measured and C is sought, thus the α coefficient must be calculated or experimentally determined for each set of operating conditions (E_0 and ψ).

The success of the empirical approach using experimentally determined α values has been good in many binary systems, and Ingersoll et al [393] and Ziebold and Ogilvie [123,394] have obtained good results in some ternary systems. In addition, Bence and Albee [395] have been successful in applying the technique to complex geological samples, for which this approach serves as the basis of the program, as it does for the one by Gast and Glover [396]. The latter two have experimentally determined the α correction parameters for ten elements in their corresponding oxides; however, the values are only applicable up to values of $E_0 = 15$ kV and $\psi = 52.5$ deg. Albee and Ray [400] have recently extended the coverage to include 36 elements at 15 and 20 kV for $\psi = 52.5$ and 38.5 deg. They will offer the data for other E_0 and ψ values upon request.

While the most successful use of the empirical procedure has occurred when experimentally determined α values are used, it is possible to use a computer program with a ZAF scheme to calculate α . The programs by Lifshin [96] and Beaman [126] compute C from k and obtain a linear least squares fit to the C/k versus C data, from which binary α coefficients are obtained. These may be used externally in binary systems or to calculate α values for use in multicomponent systems.

The complete computer programs available today based on ZAF corrections are long (25,000 words) and, consequently, expensive to run and are not always easy

to use, particularly if the continuum fluorescence correction is part of the program. This problem could be circumvented by using a computer program that simply stored all the possible binary α values which had been computed in another ZAF program. In any particular problem, an equation $\left(\frac{1-k}{k} = \alpha \frac{1-C}{C}\right)$ would be

generated for each of the analyzed elements by using Eq 6 for each α_k ; these equations would then be solved simultaneously for the concentrations. There are some problems associated with such an approach. α depends on E_0 and ψ , and for complete atomic number coverage a 92 by 92 α array would be required for each E_0 , ψ combination. While the number of different ψ values in commercial EPAs is limited, the possibilities in SEMs are enormous. Linear interpolation between E_0 (at a given ψ) values would be satisfactory in most cases, but a polynomial fit to the α versus E_0 data would give better results. Unfortunately, k/C versus C data are not always linear, and the physical assumptions implicit in the expression for α_k may lead to errors in some multicomponent systems. Despite the difficulties, such a procedure could lead to much more efficient correction and would be useful in many applications.

Historical Summary of Attainable Accuracy/ The discussion on quantitative analysis can be appropriately summarized by indicating some of the results obtained during the last seven years. Table 26 is a historical summary of some of the attempts made by various researchers and users groups to establish values for expected quantitative accuracy. Most of the work has been directed at technique evaluation and has involved the conversion of a large number of experimental probe ratios to compositions primarily in binary alloys of known chemical composition.

A statistical approach has been preferred, regardless of its lack of attention to the validity of a particular technique, because (1) it is possible to study a broad range of Z , E_0 , and ψ values and (2) good experimental data cannot be expected without a thorough understanding of the sources of experimental error described earlier. While instrumentation has improved over the years, understanding, patience, and desire are still required of an analyst seeking accurate k values. The statistical approach presumes that many of the data are good but that some are not and minimizes the influence of operator or instrumental inadequacies or errors in the independent chemical analyses. The need for an appreciable accumulation of carefully characterized alloys and accompanying probe measurements has been vehemently stressed for sometime by

Heinrich. The amount of such information is increasing slowly, in the United States primarily through the efforts of the local users groups (interlaboratory specimens) and the NBS, which provides carefully characterized alloys for probe analyses (W-Mo, Au-Ag, Cu-Au).

Some generalizations are possible from the table. The relative accuracy (σ/C) has decreased linearly from 5 to 6 percent in 1963 to 1 to 2 percent in 1970. When the characteristic fluorescence correction predominates or when there are large absorption corrections or when the concentration is less than 10 percent or when $Z(A) < 10$ or any combination of them occurs, larger errors are often encountered. The improvement to date certainly justifies the effort and one would expect that a relative accuracy of 1 percent will be commonplace ($Z > 10$, $C < 10$ percent) in the not too distant future. The ability to accurately determine in about 1 h the chemical composition of 1 to 10 μm^3 of material, with a spatial resolution of 1 μm , using pure material standards is a remarkable feat.

It is unlikely that further improvements in accuracy will occur soon, but it is certain that the volume analyzed will diminish in the near future as the several techniques are combined within a single instrument. More accurate and complete characterization of surfaces will be possible, as will lower detection limits. The potential in areas such as material failure analysis and development, ecology, human and plant pathology, criminology, and geology are indeed staggering.

Notes Added in Proof

C. A. Andersen has developed an expression for use in quantitative ion microprobe analysis which he used in the analyses of several minerals where he attained a relative accuracy of better than 10%. The method has been incorporated into a computer program. Their results were presented at the Sixth National Conference on Electron Probe Analysis, July 1971, Pittsburgh, Pa. and included (Paper 8) in the proceedings. At this same meeting J. Bombard (Paper 3) reported that Si escape peaks can be troublesome in trace analyzer using energy dispersive spectrometer. Jaklrvic and Goulding (Paper 1) reported detecting C, N, O and F with an EDS. Short (Paper 53) described an electronic stabilizer that eliminated the problems due to pulse amplitude shifts up to 50000 cps in a gas flow proportional detector.

A fine review paper entitled Auger Electron Spectroscopy by C. C. Chang has recently been published: Surface Science, Vol. 25, 1971, pp. 53-79.

APPENDIX 1—Definition of Symbols

Symbols listed in alphabetical order

<i>A</i>	Atomic weight of element A	μ/ρ	Mass absorption coefficient, cm ² /g
<i>A</i>	Absorption correction	$(\mu/\rho)_{\text{target}}^A$	$\sum_i^N C_i (\mu/\rho)_i^A$
<i>A, B, ..., N</i>	Elements A, B, ..., N in an N-components alloys	<i>m_t</i>	Observed count rate at time <i>t</i>
$\text{\AA}$	Angstrom, 10 ⁻⁸ cm	<i>n</i>	In Braggs law, the order of diffraction
α	Half-angle between limiting ray and the optical axis	<i>n</i>	Number of components in a system
α	Empirical parameter appearing in the Ziebold and Ogilvie expression relating <i>C</i> and <i>k</i>	<i>n</i>	Number of determinations
AES	Auger electron spectroscopy	<i>n</i>	True count rate, cps
<i>B</i>	Spectral background intensity, counts or cps	nA	Nanoamperes, 10 ⁻⁹ A
<i>B°</i>	Spectral background intensity from a standard	<i>n_K</i>	Total number of K ionizations produced per unit incident electron
<i>B'</i>	Spectral background intensity from an unknown	<i>N</i>	Counts; less often counting rate = impulses/time
β	Gun brightness, A/cm ² /sr	$\bar{N}$	Mean count
<i>C_A</i>	Concentration of the analyzed element	<i>N₀</i>	Avogadro's number, 6.02 × 10 ⁻²³ atoms per mole
<i>C_B, C_C, ..., C_N</i>	Concentration of the remaining elements	nsp	Nonself-prolonging
<i>C(DL)</i>	Concentration corresponding to the detectability limit	ω	Fluorescence yield
<i>cf</i>	Continuous fluorescence	Ω	Effective crystal area/ <i>r</i> ²
cps	Counts per second	<i>P</i>	Spectral peak intensity, counts or cps
CRT	Cathode ray tube	<i>P'</i>	Spectral peak intensity from an unknown
<i>C_s</i>	Spherical aberration coefficient, cm	<i>P°</i>	Spectral peak intensity from a standard
<i>X'</i>	$(\text{csc}\psi)(\mu/\rho)_{\text{target}}^A$	<i>P_{ij}</i>	In the Reed equation, <i>P_{KK}</i> = <i>P_{LL}</i> = 1, <i>P_{LK}</i> = 4.2, <i>P_{KL}</i> = 0.24
<i>X°</i>	$(\text{csc}\psi)(\mu/\rho)_A^A$	ppm	Parts per million by weight
<i>d</i>	Electron beam diameter at the target surface	<i>P/B</i>	Peak to background ratio; signal to noise
<i>d</i>	Lattice spacing in a diffracting crystal	ψ	The superscript prime refers to the unknown material
<i>d_g</i>	Geometric electron beam diameter	ϕ (0)	X-ray take-off angle; that angle the emerging X-ray beam makes with the specimen surface
<i>dn_K</i>	Number of K ionizations produced per unit path length <i>dx</i>	ϕ (ρz)	Value of ϕ (ρz) at the surface (zero depth) of a target
<i>d_s</i>	That portion of the actual beam diameter caused by spherical aberration	QM	Distribution in depth of primary X-radiation in a target
<i>dE/dx</i>	Energy loss per increment of path length	<i>Q_K</i> (<i>E</i>)	Quantitative metallography
<i>e</i>	Charge of an electron, 1.6 × 10 ⁻¹⁹ C		K ionization cross section of A atoms for electrons; a function of the energy <i>E</i> of the electron
ϵ	Average energy required to produce an electron-hole pair	<i>R</i>	Electron range; often assumed to be the lateral diffusion of the primary electron beam for <i>E</i> = <i>e_c</i>
ϵ	Effective take-off angle	<i>R</i>	Peak to background ratio, <i>P/B</i>
<i>E</i>	Instantaneous energy of the electron	<i>R</i>	Radius of the Rowland circle
EBS	Electron beam scanning	<i>R</i>	Backscattered electron correction or backscattered coefficient; represents the fraction of the total possible ionization that actually occurs
<i>E_c</i>	Excitation potential of the atom; energy corresponding to the absorption edge	<i>R_B</i>	Bethe range
EDS	Energy dispersive spectrometer (spectrometry)	RBC	Red blood cell
EDX	Energy dispersive X-ray analysis	<i>R_X</i>	X-ray resolution; includes lateral spread <i>R</i> and electron beam diameter <i>d</i>
<i>E_n</i>	Noise contribution to the total resolution of an EDS	<i>r</i>	Target to crystal distance
<i>E₀</i>	High voltage on the electron gun, that is, acceleration potential in kV	ρ	Density, g/cm ³
<i>E_p</i>	Proportional detector contribution to the total resolution of an EDS	ρx	Mass thickness, g/cm ²
EPA	Electron probe analyzer (analysis)	$\rho^0 N_0/A$	Number of A atoms per unit volume, where ρ^0 is the density of the pure material, <i>N₀</i> is Avogadro's number, and <i>A</i> is the atomic weight of element A
EPASA	Electron Probe Analysis Society of America		
η	Backscattered electron fraction (number of backscattered electrons/number of incident electrons)	<i>S</i>	Stopping power <i>S</i> = $-dE/pdx$, or energy loss correction
eV	Electron volt		
ΔE_p	Theoretical resolution of an EDS using a flow proportional detector	<i>S</i>	$1/\bar{k} \left(\frac{\sum_i (\bar{k} - k_i)^2}{n-1} \right)^{1/2} \left(\frac{P' + B'}{(P' - B')^2} + \frac{P^0 + B^0}{(P^0 - B^0)^2} \right)^{1/2}$
<i>E_{Si}</i>	Silicon detector contribution to the total resolution of an EDS	SEM	Scanning electron microscope (microscopy)
ΔE_{Si}	Theoretical resolution of an EDS using a Si detector	SWL	Short wavelength limit, depends on <i>E₀</i>
<i>F</i>	Fano factor	sp	Self-prolonging
<i>F</i>	Characteristic fluorescence correction	σ	Voltage factor in the absorption correction, $C(10)^{5/(E_0^n - E_c^n)}$
FET	Field effect transistor	σ	Standard deviation
<i>F</i> (O)	Total generated X-ray intensity by the primary beam	σ_k	Standard deviation in the probe ratio
FWHM	Full width at one-half maximum intensity of a spectral line	σ^2	Variance
FWTM	Full width at one-tenth maximum intensity of a spectral line	<i>t</i>	Tilt angle for a specimen in an SEM
<i>f</i> (<i>X</i>)	Fraction of the total generated intensity <i>F</i> (O) that is emitted at the surface of a target	<i>T</i>	Temperature
γ	Ratio of the emitted intensity due to characteristic fluorescence excitation to the emitted intensity due to electron excitation	τ	Deadtime, usually μ s
<i>h</i>	1.2 <i>A</i> / <i>Z</i> ²	TEM	Transmission electron microscope (microscopy)
<i>i</i>	beam current, or nA	TEP	Transport equation program
<i>I</i>	X-ray intensity, transmitted by or incident upon a thin film	TF	Thermionic field emission (refers to gun)
<i>I_{cf}</i>	Emitted X-radiation due to excitation by the continuous X-ray spectrum	θ	Bragg angle, where $n\lambda = 2d\sin\theta$
<i>I_f</i>	Intensity emitted by a composite target due to characteristic fluorescence	θ	Acute angle between the incident beam and the specimen surface
IMA	Ion mass analyzer or ion microprobe analyzer	UFO	Unidentified flying object
<i>i₀</i>	Current density, A/cm ²	<i>U</i>	Overvoltage = <i>E₀</i> / <i>E_c</i>
<i>I_p</i>	Intensity emitted by a composite target due to primary electron excitation	<i>W</i>	<i>E</i> / <i>E₀</i>
<i>I_t</i>	Total emitted X-ray intensity	<i>W_c</i>	<i>E_c</i> / <i>E₀</i>
<i>J</i>	Mean ionization potential	WDS	Wavelength dispersive spectrometer
<i>k</i>	X-ray intensity ratio; the intensity from an unknown divided by that from a known standard; the measured concentration	<i>x</i>	Film thickness, cm
<i>k</i> (cal)	Calculated X-ray intensity	<i>x</i>	Electron trajectory (electron path length)
<i>k</i> (exp)	Experimentally measured X-ray intensity ratio	<i>x</i>	Absorption path length for X-radiation
K, L, M	Atomic shell designations	<i>Z</i>	Atomic number
kV	Kilovolts	$\bar{z}$	Depth below the target surface
<i>K</i>	Kramers constant	$\bar{Z}$	Atomic number correction
λ	Wavelength of X-radiation	<i>Z/A</i>	Number of electrons per unit mass
<i>m</i>	Observed count rate, cps	$\bar{Z}/A$	Atomic number ($\bar{Z}$), absorption (<i>A</i>), and characteristic fluorescence (<i>F</i>), corrections, refers to a complete correction scheme
μ m	Micrometer, 10 ⁻⁴ cm	<i>0</i>	The superscript zero refers to the standard material
MC	Monte Carlo techniques		
MCA	Multichannel analyzer		
<i>m/e</i>	Mass to charge ratio		

Symbols in order of their appearance in the text

EPA	Electron probe analyzer (analysis)
UFO	Unidentified flying object
SEM	Scanning electron microscope (microscopy)
TEM	Transmission electron microscope (microscopy)
EDS	Energy dispersive spectrometer (spectrometry)
K,L,M	Atomic shell designations
μm	Micrometer, 10^{-4} cm
Z	Atomic number
$\text{\AA}$	Angstrom, 10^{-8} cm
ppm	Parts per million by weight
kV	Kilovolts
d_p	Geometric electron beam diameter
d_s	That portion of the actual beam diameter caused by spherical aberration
α	Half-angle between limiting ray and the optical axis
C_s	Spherical aberration coefficient, cm
i	Beam current, A or nA
d	The electron beam diameter at the target surface
β	Gun brightness, $\text{A}/\text{cm}^2/\text{sr}$
E_0	High voltage on the electron gun, that is, acceleration potential in kV
k	Boltzman constant, 1.38×10^{-23} J/mol $\cdot$ $^{\circ}\text{K}$
e	Charge of an electron, 1.6×10^{-19} C
T	Temperature
i_0	Current density, A/cm^2
nA	Nanoamperes, 10^{-9} A
cps	Counts per second
TF	Thermionic field emission (refers to gun)
ρ	Density, g/cm^3
x	Film thickness, cm
ρx	Mass thickness, g/cm^2
R	Electron range; often assumed to be the lateral diffusion of the primary electron beam for $E = E_c$
E_c	Excitation potential of the atom; energy corresponding to the absorption edge
E	Instantaneous energy of the electron
dE/dx	Energy loss per increment of path length
N_0	Avogadro's number, 6.02×10^{23} atoms per mole
A	Atomic weight of element A
I	Mean ionization potential
R_B	Bethe range
S	Stopping power $S = -dE/\rho dx$
R_X	X-ray resolution; includes lateral spread R and electron beam diameter d
P	Spectral peak intensity, counts or cps
B	Spectral background intensity, counts or cps
P/B	Peak to background ratio; signal to noise
WDS	Wavelength dispersive spectrometer
n	In Bragg's law, the order of diffraction
λ	Wavelength of the radiation
d	Lattice spacing in a diffracting crystal
θ	Bragg angle, where $n\lambda = 2d\sin\theta$
R	Radius of the Rowland circle
ψ	The X-ray take-off angle; that angle the emerging X-ray beam makes with the sample surface
EBS	Electron beam scanning
EDX	Energy dispersive X-ray analysis
eV	Electron volt
FET	Field effect transistor
MCA	Multichannel analyzer
CRT	Cathode ray tube
FWHM	Full width at one-half maximum intensity of a spectral line
FTWM	Full width at one-tenth maximum intensity of a spectral line
F	Fano factor
σ	Standard deviation
ϵ	Average energy required to produce an electron-hole pair
E_{Si}	Silicon detector contribution to the total resolution of an EDS
E_n	Noise contribution to the total resolution of an EDS
E_p	Proportional detector contribution to the total resolution of an EDS
ΔE_{Si}	Theoretical resolution of an EDS using a Si detector
ΔE_p	Theoretical resolution of an EDS using a flow proportional detector
$^{\circ}$	The superscript prime refers to the unknown material
0	The superscript zero refers to the standard material
k	X-ray intensity ratio; the intensity from an unknown divided by that from a known standard; the measured concentration
n	Number of components in a system
$k(\text{exp})$	Experimentally measured X-ray intensity ratio
$k(\text{cal})$	Calculated X-ray intensity ratio
σ	Voltage factor in the absorption correction, $C(10)^5/(E_0^n - E_c^n)$
C_A	Concentration of the analyzed element
$C_B, C_C, \dots, C_N$	Concentration of the remaining elements
α	Empirical parameter appearing in the Ziebold and Ogilvie expression relating C and k
ϵ	Effective take-off angle

θ	Acute angle between the incident beam and the specimen surface
$f(x)$	Fraction of the total generated intensity $F(0)$ that is emitted at the surface of a target
t	Tilt angle for a specimen in an SEM
P'	Spectral peak intensity from an unknown
P°	Spectral peak intensity from a standard
B'	Spectral background intensity from an unknown
B°	Spectral background intensity from a standard
σ_k	Standard deviation in the probe ratio
$C(DL)$	Concentration corresponding to the detectability limit
n	Number of determinations
m/e	Mass to charge ratio
AES	Auger electron spectroscopy
ω	Fluorescence yield
IMA	Ion mass analyzer or ion microprobe analyzer
EPASA	Electron Probe Analysis Society of America
ZAF	Atomic number (Z), absorption (A), and characteristic fluorescence (F) corrections, referring to a complete correction scheme
QM	Quantitative metallography
RBC	Red blood cell
N	Counts; less often counting rate = impulses/time
$\bar{N}$	Mean count
σ^2	Variance
R	Peak to background ratio, P/B
$(\mu/\rho)_i^j$	Mass absorption coefficient in cm^2/g ; the absorption of i radiation by element j
$F(0)$	Total generated X-ray intensity by the primary beam
m_t	Observed count rate at time t
m	Observed count rate, cps
n	True count rate, cps
τ	Deadtime, usually μs
nsp	Nonself-prolonging
sp	Self-prolonging
S	$1/\bar{k} \left(\frac{\sum (k - k_i)^2}{n - 1} \right)^{1/2} \left/ \left(\frac{P' + B'}{(P' - B')^2} + \frac{P^0 + B^0}{(P^0 - B^0)^2} \right)^{1/2} \right.$
$\phi(\rho z)$	Distribution in depth of primary X-radiation in a target
x	Electron trajectory (electron path length)
Z/A	Number of electrons per unit mass
R	Backscattered electron correction (backscatter coefficient); represents the fraction of the total possible ionization that actually occurs
Z	Atomic number correction
z	Depth below the target surface
$\phi(0)$	Value of $\phi(\rho z)$ at the surface (zero depth) of a target
I	X-ray intensity transmitted by X-radiation incident upon a thin film
x	Absorption path length for X-rays
A	Absorption correction
F	Characteristic fluorescence correction
I_f	Intensity emitted by a composite target due to characteristic fluorescence
I_p	Intensity emitted by a composite target due to primary electron excitation
Ω	Effective crystal area/ r^2
r	Target to crystal distance
$A, B, \dots, N$	Elements A, B, ..., N in an N-component alloy
$(\mu/\rho)_{\text{target}}^A$	$\sum_i^N C_i (\mu/\rho)_i^A$
χ'	$(\text{csc}\psi)(\mu/\rho)_{\text{target}}^A$
χ^0	$(\text{csc}\psi)(\mu/\rho)_A^A$
I_e	Emitted X-radiation due to excitation by the continuous X-ray spectrum
I_t	Total emitted X-ray intensity
γ	Ratio of the emitted intensity due to characteristic fluorescence excitation to the emitted intensity due to electron excitation
h	$1.2A/Z^2$
U	Overvoltage = E_0/E_c
P_{ij}	In the Reed equation, $P_{KK} = P_{LL} = 1$; $P_{LK} = 4.2$; $P_{KL} = 0.24$
dn_K	Number of k ionizations produced per unit path length dx
$Q_K(E)$	K ionization cross section of A atoms for electrons; a function of the energy, E , of the electron.
$\rho^0 N_0/A$	Number of A atoms per unit volume, where ρ^0 is the density of the pure material, N_0 is Avogadro's number, and A is the atomic weight of element A
n_K	Total number of K ionizations produced per incident electron
η	Backscattered electron fraction (backscattered electrons/incident electrons)
W	E/E_0
W_c	E_c/E_0
cf	Continuous fluorescence
SWL	Short wavelength limit; only a function of the accelerating potential, E_0
K	Kramers constant
TEP	Transport equation program
MC	Monte Carlo techniques

APPENDIX 2—Complete Hand Calculations for the Cu-Co Al Alloy System

In this appendix an example problem in the Cu-Co-Al ternary alloy system is worked out in detail to illustrate the use of the physical data and theoretical expressions presented in the text. The experimental information consists simply of three X-ray intensity ratios corrected for background, deadtime and drift, the acceleration potential, and the X-ray take-off angle.

$k(\text{Al}) = 0.098$
 $k(\text{Cu}) = 0.492$
 $k(\text{Co}) = 0.011$
 accelerating potential = 25 kV
 $\psi = 18^\circ$
 $\csc \psi = 3.2361$

After the hand calculations are completed an example of the input to and output from a computer program based on a classical ZAF correction scheme is presented. A flow diagram of the calculation process is shown in Fig. 56.

It is convenient to first calculate and tabulate all of the quantities that are independent of composition. Atomic weight and E_c values can be found in Ref 402; J values are listed in Table 24; ω and r values are plotted in Fig 52 and can be found in Refs 45, 351 and 350, 403, respectively. The mass absorption coefficients most commonly used are Heinrich's [350] and for this alloy are as follows:

Analyzed Element	Absorber		
	Al	Co	Cu
Al	385.7	4330.8	5376.8
Co	75.0	64.9	80.6
Cu	49.6	341.2	53.7

A σ value for each element is calculated from

$$\sigma = \frac{450,000}{E_0^{1.65} - E_c^{1.65}}$$

$f(\chi)^0$ is calculated from Eq 24:

$$f(\chi)^0 = \frac{1 + h^0}{\left(1 + \frac{\chi^0}{\sigma}\right) \left(1 + h^0 \left(1 + \frac{\chi^0}{\sigma}\right)\right)}$$

where

$$h^0 = 1.2A/Z^2$$

$$\chi^0 = (\csc \psi)(\mu/\rho)_A^{A K\alpha} = (\csc \psi)(u)_A^{A K\alpha}$$

Henceforth, u_i^i will be used to represent the mass absorption coefficient $(\mu/\rho)_i^i$. The elemental data are given in Table 27. A

cross through a value means that information will not be needed in the calculations.

Using the values of χ^0 , h^0 , and σ given above, $f(\chi)^0$ is as follows:

Element	$1 + h^0$	$1 + (\chi^0/\sigma)$	$(1 + h^0)(1 + \chi^0/\sigma)$	$f(\chi)^0$
Al	1.19	1.556	1.296	0.590
Co	1.097	1.081	1.105	0.918
Cu	1.091	1.064	1.097	0.935

The complete correction is given by Eq 20,

$$C_A = K_A \left(\frac{F(0)^0}{F(0)'} \right) \left(\frac{f(\chi)^0}{f(\chi)'} \right) \left(\frac{1}{1 + \sum_{j=B}^N \gamma_j^A} \right)$$

The analyzed element, A, will be in turn Al, Co, and Cu, and the following expressions must be evaluated for each:

$$\chi'(A) = \csc \psi [u_A^{A K\alpha} C(A) + u_B^{A K\alpha} C(B) + u_C^{A K\alpha} C(C)]$$

$$h' = h(\text{Al})C(\text{Al}) + h(\text{Co})C(\text{Co}) + h(\text{Cu})C(\text{Cu})$$

$$R'(A) = R_A(A)C(A) + R_A(B)C(B) + R_A(C)C(C)$$

$$S'(A) = S_A(A)C(A) + S_A(B)C(B) + S_A(C)C(C)$$

$$F(0)' = R'/S'$$

$$F(0)^0 = R^0/S^0$$

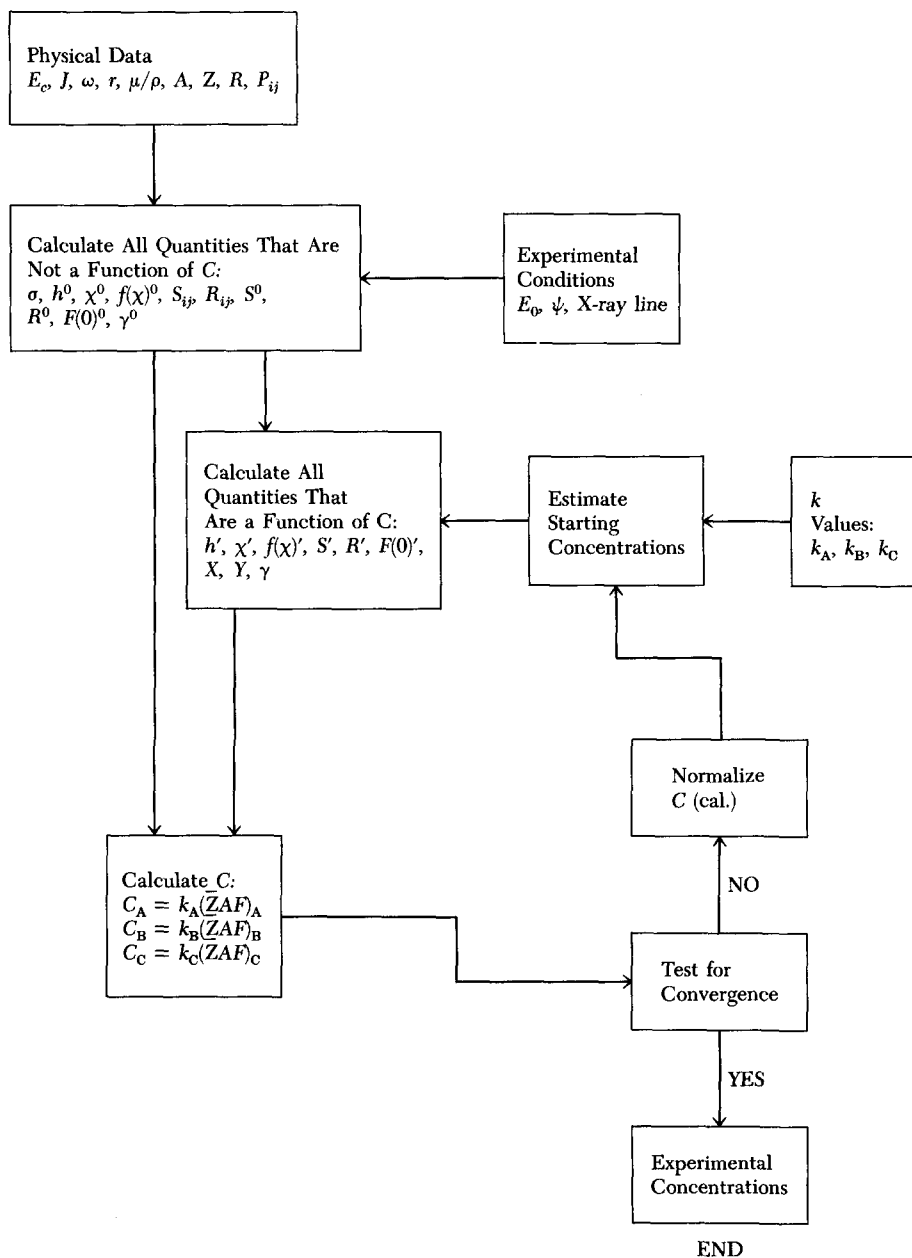


Fig. 56—Flow diagram of the ZAF calculation process used in quantitative microanalysis.

In the calculation of S' and R' , S^0 and R^0 arrays must be constructed, since $S'(A)$ and $R'(A)$ are functions of $E_c(A)$. For example, $R_A(B)$ depends on $Z(B)$ and $U(A)$ and not on $U(B)$. The $R_{Al}(Al, Co, Cu)$, $R_{Co}(Al, Co, Cu)$, and $R_{Cu}(Al, Co, Cu)$ values can be obtained from linear interpolation in terms of Z and $1/U$ using the R data of Table 23.

Analyzed Element (A)			R^0 Array		
Z	E_c	$1/U$	Al	Co	Cu
13	1.56	0.062	Al	0.918	0.820
27	7.71	0.308	Co	0.945	0.866
29	8.98	0.359	Cu	0.949	0.875

The S^0 array is constructed from Eq 37,

$$S^0 = (\text{constant}) \frac{1}{E} \frac{Z}{A} \ln \frac{1.166E}{J}$$

The constant and $1/E$ terms can be disregarded in calculating S^0 , as they will cancel out when the ratio $F(0)^0/F(0)'$ is taken. Thus, S^0 can be calculated from

$$S^0 = \frac{Z}{A} \ln \frac{1.166E}{J}$$

where $E = (E_0 + E_c(A))/2$ and Z , A , and J are the values for the retarding element but E_c is the excitation potential of the analyzed element. The calculations necessary for obtaining the S^0 array are as follows:

Analyzed Element (A)				
	Z	$E_c(A)$	E	$1.166E$
Al	13	1.56	13280	15484
Co	27	7.71	16350	19064
Cu	29	8.98	16990	19810

Retarding Element			
	Al	Co	Cu
Z	13	27	29
A	26.98	58.94	63.57
Z/A	0.482	0.458	0.456
J	142	347	377

$1.166E/J$			
	Al	Co	Cu
Al	109.0	44.62	41.07
Co	134.3	54.94	50.57
Cu	139.5	57.09	52.55

$\ln(1.166E/J)$			
	Al	Co	Cu
Al	4.691	3.798	3.715
Co	4.900	4.006	3.923
Cu	4.938	4.045	3.962

S^0 Array			
	Al	Co	Cu
Al	2.261	1.739	1.694
Co	2.362	1.835	1.789
Cu	2.380	1.853	1.808

Table 27—The Elemental Parameters That are not Dependent on Concentration

Parameter	Element		
	Al	Co	Cu
Z	13	27	29
A	26.97	58.94	63.57
$E_c(\text{keV})$	1.56	7.71	8.98
$\omega(k)$	0.626	0.358	0.425
$r(k)$	12.4	8.0	7.7
$U = E_0/E_c(A)$	16.8	3.24	2.78
$h^0 = 1.2A/Z^2$	0.19	0.097	0.091
$J(\text{eV})$	142	347	377
$F(0)^0 = R^0/S^0$	0.406	0.472	0.478
σ	2244	2594	2724
$(\mu/\rho)_A^{K\alpha}$	385.7	64.9	53.7
χ^0	1248	210	174
$f(\chi)^0$	0.590	0.918	0.935
$k(\text{measured})$	0.098	0.011	0.492

$F(0)^0$ is obtained from $R_A(A)/S_A(A)$. $F_{Al}^0(0) = 0.918/2.261 = 0.406$; $F_{Co}^0(0) = 0.866/1.835 = 0.472$; $F_{Cu}^0(0) = 0.864/1.808 = 0.478$.

Only the fluorescence of Co $K\alpha$ will be calculated (neglecting the excitation of Co $K\alpha$ by Cu $K\beta$). Most of the parameters in the expression for γ are not functions of concentration. In the case of KK fluorescence $P_{ij} = P_{KK} = 1$. γ from Eq 25 is given by

$$\gamma = \left\{ 0.5P_{ij} \frac{r(\text{Co}) - 1}{r(\text{Co})} \omega(\text{Cu}) \left(\frac{\mu}{\rho} \right)_{\text{Co}}^{\text{Cu } K\alpha} \frac{A(\text{Co})}{A(\text{Cu})} \left(\frac{U(\text{Cu}) - 1}{U(\text{Co}) - 1} \right)^{1.67} \right\} C_B(X + Y)$$

Call the term in brackets γ^0 ; its value is

$$\gamma^0 = (0.5)(1) \left(\frac{8.0 - 1}{8.0} \right) (0.425)(341.2) \frac{58.94}{63.57} \left(\frac{2.78 - 1}{3.24 - 1} \right)^{1.67} = 40.12$$

therefore

$$\gamma = 40.12 C_B(X + Y)$$

X and Y are functions of concentration because of their dependence on χ' . The expressions for X and Y are

$$X = \frac{\ln \left(1 + \frac{\chi'(\text{Co})}{\chi'(\text{Cu})/\text{csc}\psi} \right)}{\chi'(\text{Co})}$$

$$Y = \frac{\ln \left(1 + \frac{\sigma(\text{Cu})}{\chi'(\text{Cu})/\text{csc}\psi} \right)}{\sigma(\text{Cu})}$$

The fluorescence correction factor for this ternary alloy system will appear only in the expression relating $k(\text{Co})$ and $C(\text{Co})$ and is as follows:

$$\left(\frac{1}{1 + \sum_{j=B}^N \gamma_j^A} \right) = \frac{1}{1 + 40.12 C(\text{Cu})(X + Y)}$$

Reed [118] has made some simplifying assumptions so that γ can be rapidly calculated from graphs and tables. He also provides a useful table for determining when the fluorescence of one radiation by another is possible, in addition to establishing guidelines as to when that fluorescence will be significant. The calculations for the alloy system are best carried out in the tabular form to follow. Because $C(A)$ appears on both sides of Eq 20, it is necessary to solve for $C(A)$ using successive approximations; that is, assume values of $C(A)$, $C(B)$, and $C(C)$ and calculate new concentration values, continuing until convergence occurs.

The various methods of solving Eq 20 for the concentration have been discussed by Beaman and Klipple in Ref 404. Here

Table 29—Calculations of the Concentrations Needed to Start Each Iteration

	Element		
	Al	Co	Cu
Original composition based on <i>k</i> values	0.160	0.020	0.820
First calculated concentration	0.555	0.008	0.437
Average of above two—starting value for second iteration	0.358	0.014	0.628
Second calculated concentration	0.486	0.010	0.504
Average of above two—starting value for third iteration	0.422	0.012	0.566
Third calculated concentration	0.463	0.010	0.527
Average of above two—starting value for fourth iteration	0.443	0.011	0.546
Fourth calculated concentration	0.454	0.010	0.536
Average of about two—starting value for fifth iteration	0.449	0.010	0.541
Fifth calculated concentration, not normalized	0.454	0.010	0.540
Starting value for sixth iteration	0.450	0.010	0.540
Sixth calculated concentration, not normalized	0.452	0.010	0.540

Table 30—The Calculation of the Fluorescence Correction Factor

	Iteration 1	Iteration 2	Iteration 3	Iteration 4	Iteration 5
χ' (Co)	256.9	253.7	252.7	252.1	252.1
χ' (Cu)	190.0	182.2	179.3	178.3	177.3
χ' (Cu)/ $\text{csc}\psi = q$	58.71	56.30	55.41	55.10	54.79
χ' (Co)/ q	4.376	4.506	4.561	4.575	4.601
$1 + (\chi' \text{ (Co)}/q) = r$	5.376	5.506	5.561	5.575	5.601
$\ln r$	1.681	1.704	1.716	1.718	1.723
$\ln r/\chi' \text{ (Co)} = X$	6.54×10^{-3}	6.72×10^{-3}	6.79×10^{-3}	6.81×10^{-3}	6.83×10^{-3}
$\sigma \text{ (Cu)}$	2724	2724	2724	2724	2724
$1 + (\sigma \text{ (Cu)}/q) = S$	5.640	5.838	5.916	5.944	5.972
$\ln S$	1.730	1.764	1.778	1.782	1.787
$\ln S/\sigma \text{ (Cu)} = Y$	0.64×10^{-3}	0.65×10^{-3}	0.65×10^{-3}	0.65×10^{-3}	0.66×10^{-3}
$X + Y$	7.2×10^{-3}	7.37×10^{-3}	7.44×10^{-3}	7.46×10^{-3}	7.49×10^{-3}
$C \text{ (Cu)}$	0.82	0.628	0.566	0.546	0.541
$(40.12) C \text{ (Cu)} (X + Y) = \gamma$	0.237	0.186	0.169	0.163	0.163
$1 + \gamma$	1.237	1.186	1.169	1.163	1.163
$1/(1 + \gamma) = F$	0.808	0.843	0.855	0.860	0.860

Table 31—Output from a Computer Program Written by Duncumb and Jones, Ref. 127.

AL-CU-CO TERNARY ALLOY SYSTEM AT 25 KV				7/15/71
CAMECA COSEC = 3.2361				ABS COEFF 1
SYSTEM ALK 1 CUK 1 COK 1				
ANALYSIS NO. 1				
	KV	MEASURED	TRUE	
AL	25.0	0.098	0.452	
CU	25.0	0.492	0.540	
CO	25.0	0.011	0.010	
		TOTAL	1.002	

we will use the simplest method, which has also been shown to work the best, namely, one of calculating all the parameters that are functions of concentration and then solving Eq 20 for each element in the system. The newly calculated concentrations will be used to estimate a new set of concentrations and the calculations performed again, that is, iteration will be carried out. The normalized probe ratios will be used as the initial concentrations.

Since $k(\text{Al}) + k(\text{Co}) + k(\text{Cu}) = 0.601$. The estimated concentrations thus become

$$C(\text{Al}) = 0.098/0.601 = 0.16,$$

$$C(\text{Co}) = 0.011/0.601 = 0.02,$$

and

$$C(\text{Cu}) = 0.492/0.601 = 0.82.$$

These values and the parameters calculated previously are all that is needed to complete the first iteration.

After each iteration it is necessary to

make a new estimate of the concentrations for use in the next iteration. A simple averaging procedure is used rather than the more complex, rapid, and efficient Wegstein method described elsewhere [126,405]. The averaging process and the results of the successive iterations are in listed Table 29. The complete calculation sequence is presented in Table 28 for each of the six successive iterations. The calculations of the fluorescence correction factor, *F*, appear in Table 30.

Note that the ZAF factors for Co and Cu do not change sufficiently in the fourth and fifth iterations to alter the calculated concentrations of 1 percent Co and 54 percent Cu. The Al concentration converges slowly, so a final iteration is made, using 1 percent Co, 54 percent Cu, and the balance Al as the starting composition. The final calculated values are 45.2 percent Al, 1 percent Co, and 54 percent Cu. The magnitude and nature of the correction in this system are evident from the last iteration and can be summarized as follows:

Element	<i>k</i>	$\bar{Z}$	<i>A</i>	<i>F</i>	ZAF	<i>C</i>
Al	0.098	0.93	4.99	1.0	4.62	0.452
Co	0.011	1.08	1.02	0.86	0.94	0.010
Cu	0.492	1.09	1.00	1.0	1.10	0.540
Total	0.621	...	...	...	...	1.002

The absorption correction predominates in the case of Al. For Co the large atomic number correction is more than offset by the large fluorescence correction, so $C < k$. The probe ratio of 49.2 percent Cu is corrected to 54 percent Cu as a result of the large atomic number correction.

To collect the needed data, make the necessary decisions, and perform by hand the calculations just completed would take one investigator about one day. The following illustrates the input cards required for the computer program written by Duncumb and Jones [127]

Al-Cu-Co TERNARY ALLOY AT 25kV
CAMECA 3.2361
AlKl CuKl CoKl
25.0
0.098 0.492 0.011

first card: system designation
second card: instrument type and $\text{csc}\psi$
third card: element and X-ray line designation, for example, AlKl means Al K α radiation

fourth card: acceleration potential
fifth card: experimentally measured probe ratios given in the order established on the third card.

These input cards can be prepared in less than 1 min. The output in Table 31 is self-explanatory and was obtained from an IBM 1130 in 30 s at an approximate cost of \$0.10.

Acknowledgments

We are indebted to the following persons, who critically reviewed various sections of the paper: C. A. Andersen, Applied Research Laboratories; R. Lewis, Cameca Instruments Inc.; P. W. Palmberg, Physical Electronics Industries Inc.; H. P. Rasmussen, Michigan State University; J. C. Russ, EDAX Laboratories; and V. E. Shull, Michigan State University. We must especially acknowledge the following persons, who reviewed the entire manuscript: J. L. Bomback, U. S. Steel Fundamental Research Laboratory; E. Lifshin, General Electric Corporate Research and Development; and J. Tabock, Ford Motor Co.

This work could not have been completed without the willing cooperation of The Dow Chemical Co. and the Westinghouse Electric Corp.

Last, but certainly not the least, the authors must thank Lynna Beaman and Flora Isasi for their encouragement, assistance and at times even tolerance.

REFERENCE: Beaman, D. R. and Isasi, J. A., "Electron Beam Microanalysis: The Fundamentals and Applications," *ASTM STP 506*, American Society for Testing and Materials, 1972, pp. 1-80.

ABSTRACT: This review describes the examination of micro-volumes of material for the purpose of determining their chemistry, structure, and morphology. The techniques discussed encompass a broad range of capability, such as electron probe analysis (EPA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), ion mass analysis (IMA), Auger electron spectroscopy (AES), and combinations thereof. These techniques, their range of applicability as well as the desirability and feasibility of combining them within a single instrument are discussed. A major emphasis is placed on electron probe analysis because of the broad application and extensive theoretical development it has undergone during the past dozen years.

The fundamentals of accurate quantitative analysis using electron beam excitation are presented. The accuracy, precision, and resolution capabilities of the SEM*EDS combination are compared with the conventional EPA*WDS arrangement, and recommendations as to the most desirable combinations are made. Electron interactions in solids and their effect on spatial resolution are described, and the significant enhancement of performance resulting from the use of the new electron guns—lanthanum hexaboride and field emission—is explained.

The experimental problems associated with the measurement of X-ray intensity ratios in EPA are explained. A complete example of quantitative analysis in a ternary system is fully worked out and an entire section is devoted to the initial needs of the novice. The role and feasibility of automation in the instrument of the future is pursued. A number of outstanding applications in the following fields are included: materials research, geology, archaeology, forensic science, ecology, numismatics, and biology.

KEY WORDS: chemical analysis, microanalysis, volumetric analysis, microscopy, spectroscopy, electron probes, electron beams, irradiation, ion microscopes, Auger electrons, X-rays, electron microscopy, scanning, transmission, electron guns, brightness, wave dispersion, morphology, microstructure, crystal structure

*SEM—energy dispersive spectrometer

EPA—Wavelength dispersive spectrometer

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