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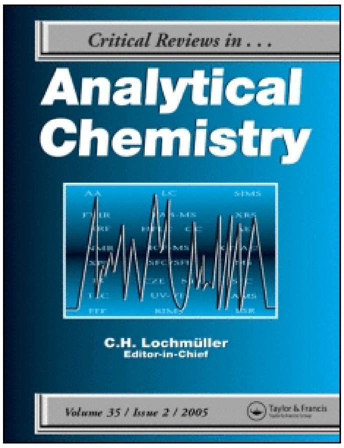

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G. L. Macdonald; L. S. Birks

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RECENT DEVELOPMENTS IN X-RAY SPECTROMETRY

Author: **G. L. Macdonald**
Central Materials Laboratory
Mullard Mitcham
Mitcham, Surrey
England

Referee: L. S. Birks
U.S. Naval Research Laboratory
Nuclear Science Division
Washington, D.C.

TABLE OF CONTENTS

I. INTRODUCTION

Although X-ray spectrometry has a history covering nearly 70 years,[1] it is only within the last 25 that the technique has added significantly to the armory of weapons available to the analytical chemist. The reasons for the rapid increase in the use of the technique in recent years are not hard to find. A very large proportion of the requirements for inorganic elemental analysis can be met by X-ray spectrometry: All of the elements from uranium down to sodium and, with limitations, on to beryllium, can be detected and determined at concentrations from 100% to below 1 ppm in favorable cases, and with a relative precision, when necessary, of 0.1% for the higher concentrations. The methods are inherently nondestructive in most cases, and samples are almost always available for repetitive checks, or for further analysis by other means. The sample state can be solid, liquid, or gaseous and in the first case can take a very wide variety of forms. Qualitative spectra are easily interpreted and quantitative precision is largely within the analyst's control, although accuracy, as always, is more difficult to ensure.

With this vast potential in its favor it is not, at first sight, easy to see why the technique took so long to receive general acceptance. The answer lies in the fact that even the simplest X-ray spectrometer today requires a technology and manufacturing sophistication that just did not exist 30 years ago. Even now, a large proportion of the very recent developments have been on the instrumental side, as will be apparent from the following pages. Manufacturers have been consolidating past gains by producing anything from small portable radioisotope-based spectrometers, for geological field work, to large automatic instruments with computer control, both of instrument parameters and data handling, for process control in cement or steel works. Innovators, meanwhile, have been working on X-ray excitation, dispersion, and detection to fill in the gaps, extend the range, or reorient the technique to satisfy new analytical requirements.

Hydrogen and helium are the only two elements that cannot be detected by any X-ray spectrometer, but the utility of the technique for determinations of the important elements from lithium to oxygen is still inadequate and workers are making only slow progress in this field.

Recent attempts to lower detection limits, both in terms of concentration and in absolute terms, have been rather more successful. Electron probe microanalysis, a technique more closely related to the original X-ray spectrometry of von Hevesy[2] and others than to X-ray fluorescence, has, since its establishment,[3] been capable of detection limits of less than 10^{-14} g. Its concentration limit, however, has been, and still is, not much better than 0.1%. It is capable, therefore, of trace analysis, but only in a specialized sense, and its very real and increasing advantages will be discussed separately. For X-ray fluorescence the limits were more like 100 μg and 100 ppm initially. Advances in indirect trace analysis by preconcentration have been reasonably successful, especially with precipitation and ion-exchange techniques. Direct methods involving more powerful X-ray tubes, better collimation, better crystals, and more detailed attention to sample preparation have all helped to lower the limits until 0.1 μg and 0.1 ppm should be achievable in many instances.

Computer technology has an impetus of its own and instrumental analysts have largely attempted to use each new development rather than to influence its course. Outside the nuclear field, X-ray spectrometry was the first analytical technique to offer an already digitized signal, and the electron probe microanalysts were the first to capitalize on the fact. One reason was that, as in the case of X-ray fluorescence, standards that matched the samples closely in composition could not be guaranteed on a micro-scale, and so relatively complex calculations based on pure-element standards were necessary. Over the years there have been progressive attempts to achieve a similar state of affairs for X-ray fluorescence and recent quantification of the primary X-ray spectrum has brought nearer the day when standards may no longer be necessary.

Even more significant is the advent of the minicomputer and the rapid drop in its cost, to a level that makes it economic to incorporate it in many X-ray spectrometers. In the normal wavelength-dispersive equipment the instrumental parameters can be computer-controlled and data-handling facilities, adequate for most purposes, can be incorporated.

The outstanding development, however, of recent years has been the semiconductor detector, and again it is the sophistication of today's technology that has raised this from being a scientific curiosity to having the status of a new branch of the art – X-ray Energy-dispersive Spectrometry (EDS) – within a few short years. Like all new techniques it still has its limitations, the worst of which is that the count rate is limited to not much more than 10^4 counts/sec at present. But it offers, as no other technique does, virtually instantaneous qualitative analysis for elements from sodium to uranium, and it marries well to a minicomputer both for acquisition and handling of the data. Relative to wavelength-dispersive spectrometers, the semiconductor detector is inherently capable of collecting signals from a large solid angle and can, therefore, operate successfully with a source of lower intensity. Any of the accepted excitation sources – electrons, protons, X-rays, and radioisotopes – can be, and are being, used. The established uses for wavelength-dispersive instruments will remain and grow, but methods employing energy-dispersive equipment will soon supplement, complement, and in a few cases replace, the older methods.

II. DISPERSION AND DETECTION

A. General

At first sight it may seem peculiar to put discussions of the dispersion and detection of X-rays before one of their excitation, but the differences between the newly developed Energy-dispersive Spectrometry (EDS) and the well-established Wavelength-dispersive Spectrometry (WDS) must be fully appreciated before a comparison of

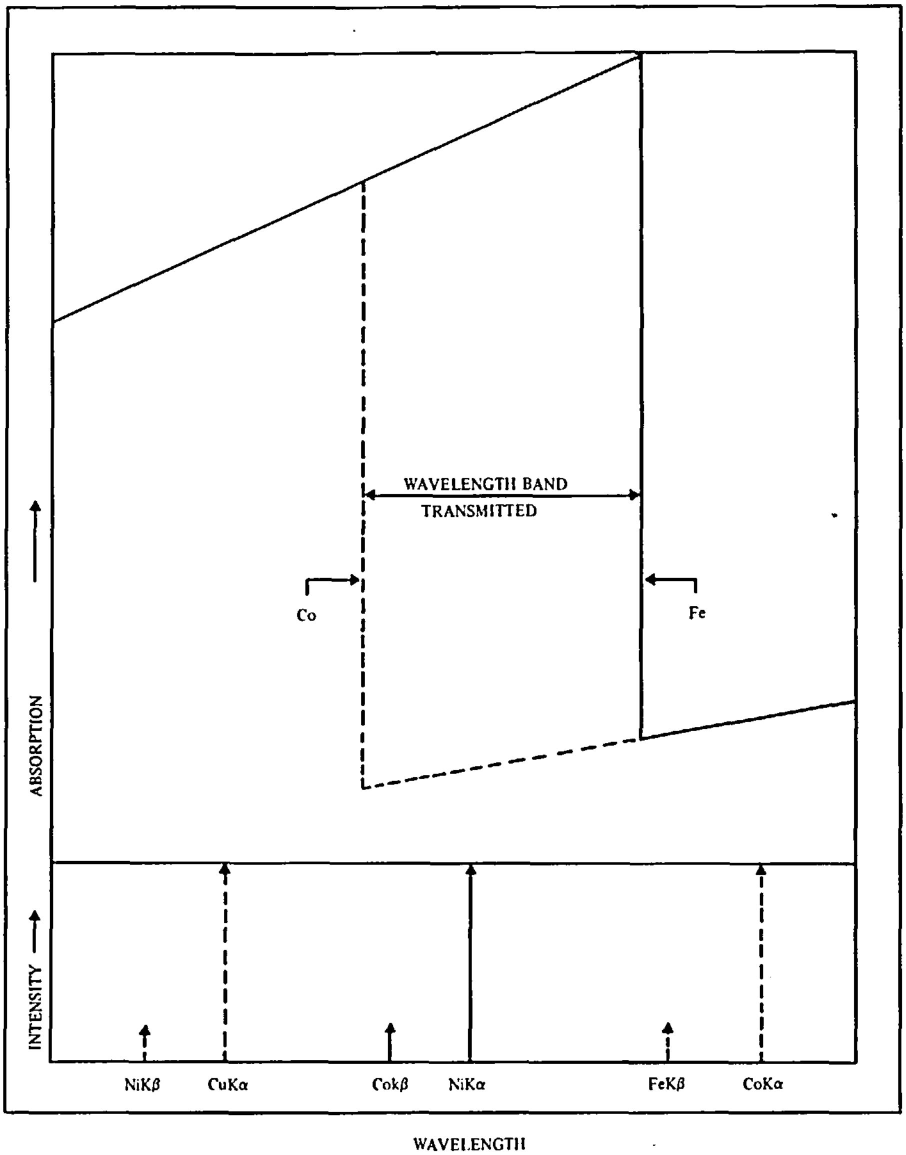

FIGURE 1. Diagrammatic representation of a Co/Fe Ross filter for the determination of Ni.

excitation modes can be seen in context. Much of the developing thought with regard to excitation has been triggered off by the arrival of EDS, although this in turn is leading to fresh appraisals of the WDS possibilities.

Although less startling, other changes in dispersion and detection have taken place in recent years and will now be outlined.

B. Nondispersive Systems

Truly nondispersive systems are now used only in the simplest of cases. Small, usually portable, spectrometers with radioisotope excitation[4] will often employ Ross[5] filters (Figure 1). These are thin foils or similar materials, usually metallic, of adjacent atomic number with X-ray absorption edges, one just above and one just below, the energy band or wavelength interval of interest. The difference between the number of quanta transmitted through the separate filters over a fixed period of time represents the wanted signal. Some instruments use the filters sequentially[6] and others have two balanced detectors, usually proportional counters, and make the two measurements simultaneously.[7]

A novel detector in this class is described by Rhodes et al.[8] The two filters are backed by phosphors with different decay times, each phosphor occupying half the window of a photomultiplier. The pulse differences between the two halves allow their electronic discrimination. Such a detector has potential advantages over proportional counters for determination of the heavier elements in the higher-energy X-ray region.

The preparation of suitable filters as suggested by Vassos et al.[9] involves electroplating onto pyrolytic graphite or collecting the appropriate metal ions on an ion-exchange membrane.

C. Scintillation-counter Dispersion and Detection

The scintillation counter, with a thallium-activated sodium iodide scintillator, continues to be the preferred detector for wavelengths shorter than 2 Å, in most conventional X-ray fluorescence work. It is usually used in tandem with a proportional counter in the intermediate region, from about 1.5 to 3 Å, where both are equally efficient.

The energy resolution of the scintillation counter is poor. It is only about 50%, or, in present day terminology, its full width at half the maximum peak height (FWHM) is about 3 keV for the MnKα line at 5.9 keV. It is used without other dispersion only in portable analyzers with radioisotope excitation.[10]

An alternative phosphor occasionally used is europium-activated cesium iodide.[11,12]

D. Proportional-counter Dispersion and Detection

Recent fundamental studies by Burek and Blake[13] of proportional counters filled with the commonly used P-10 gas (90% argon, 10% methane) showed that the linearity remained excellent over the energy range from 0.5 to 15 keV and the pressure range from 150 to 750 torr. Similar results were obtained for methane. In a few cases P-10 gas is unsuitable because the argon escape peak from one element clashes with the X-ray emission line from an element of interest. The determination of sulfur in cobalt-containing steel is an example, as is that of fluorine in a calcium-rich matrix. Loch[14] shows that neon with 30% methane, or helium with 12% carbon dioxide, is a useful alternative.

Resolution of proportional counters at around 17% or 1 keV FWHM for MnKα is three times better than that of scintillation counters but still quite inadequate for separating, say, MnKα at 5.9 keV from FeKα at 6.4 keV. Again, for simple radioisotope-based spectrometers, such resolution can often be adequate.[15] The instrument described by Gray[11] attempts to retain most of the simplicity and relatively low cost of such equipment, but to provide some flexibility. Filters can be used when desired and there is a choice between neon-, argon-, and xenon-filled proportional counters and a cesium iodide scintillation counter. With the addition of a helium path for the softer X-rays, instruments[16,17] have been designed that allow determinations of elements from calcium down to aluminum.

This last feature already requires the sacrifice of ready portability, and for most of the larger X-ray spectrometers sealed proportional counters give way to gas-flow counters allowing thinner windows to be used and hence better detection of the lighter elements to be achieved. Six-micron Mylar® (polyethylene terephthalate) has been standard window material for many years. The use of 2-μm Makrofol® (polycarbonate) was shown by Brown and Kanaris-Sotiriou[18] to have better transmission for soft X-rays combined with an acceptable lifetime of about 6 months. Polypropylene of thickness 1 μm and less is now in common use.[19]

Before the arrival of the semiconductor detector Dolby[20] proposed a solution to the resolution problem whereby convoluted spectra could be electronically separated. This network method has recently been revived and improved by Mitra and Hall[21] using modern operational amplifiers.

Sutfin and Ogilvie[22] deal with the proportional counter as an energy-dispersive device for energies below 1 keV and conclude that although it is unsatisfactory it is still the best available detector for these low energies.

To maintain the performance, and especially the resolution, of a flow counter it is necessary to maintain clean conditions in the chamber, preferably by careful filtration of the incoming gas. Even then, de Boggende et al.[23] show that carbon is deposited on the anode wire and suggest replacement of the 10% methane, which is believed to polymerize on the wire, by 10% CO_2. To prevent pulse-height shift (i.e., a change in peak voltage of the pulses produced by a given X-ray energy) at high counting rates ($>10^5$ quanta/sec), manufacturers now install thicker anode wires in their flow proportional counters.[19]

E. Wavelength Dispersion

Wavelength dispersion by diffraction from crystals or pseudocrystals has been, and still is, the commonest method for separating the polychro-

TABLE 1

Recently Proposed Crystals for Wavelength-dispersive X-ray Spectrometry

Short title	Full name	Diffracting plane	2d (Å)	Suggested for	Reference
LiF	Lithium fluoride	(422)	1.645	$\lambda<0.5$Å	25
LiF	Lithium fluoride	(420)	1.802	$\lambda<0.5$Å	25
PG	Pyrolitic graphite	(002)	6.715	P, S, Cl, K	25
SHA	Sorbitol hexa-acetate	(110)	13.98	Mg	25
RAP	Rubidium acid phthalate	(001)	26.12	F, Na, Mg	25
TlAP	Thallium acid phthalate	(001)	25.90	F, Na, Mg, O	26
–	Clinochlore	(001)	28.39	Cu, Ti, P, Al, Na, O	27

matic beam of X-rays emanating from the sample. Gilfrich,[24] discussing future developments in this area, points out not only that the resolution of the crystal spectrometer is still superior for wavelengths longer than about 0.7 Å, but that this resolution is still required in many cases. One of the classic examples quoted by him is the difference of only 48 eV between MnKα and CrKβ_1. The normal flat crystal spectrometer with a 10-cm collimator and an LiF (200) crystal has a resolution of about 10 eV in this region and will readily allow the determination of manganese at the 1% level in a stainless steel.

At the two ends of the X-ray spectrometric range, however,the situation is still not completely satisfactory and Table 1 lists some of the crystals recently proposed to improve the situation. At the short-wavelength end Jenkins,[25] following the proposals of Birks,[336,337] suggests that LiF(420) in particular is better than the commonly used LiF(220) in spite of an intensity loss of about 60%, because the angular dispersion is doubled and the 'forbidden' odd order reflections (110), (330), etc., do not occur. Moreover, the percentage of the X-ray beam intercepted by a given length of crystal at a fixed short wavelength is greater, and so some (up to 40%) of the lost intensity is effectively regained.

Both pyrolytic graphite and sorbitol hexa-acetate offer potentially higher diffracted intensities, but line breadth is excessive in the first case and crystal perfection inadequate as yet in the second. Vié le Sage and Grubis[26] recommend thallium acid phthalate in preference to the older potassium salt, or even the somewhat more up-to-date rubidium one. They claim approximately twice the reflecting power for elements from magnesium to oxygen inclusive. A slightly earlier proposal by Baun and White[27] was for clinochlore as being suitable for the 5-27 Å region. Alexandropoulos and Cohen[28] take a fresh look at a comprehensive list of crystals as possibilities for stellar spectrometers.

F. Energy Dispersion

The subject of energy dispersion has been touched on already in relation to scintillation and proportional counters, and this feature of these detectors is, of course, used in wavelength-dispersive spectrometers to prevent unwanted higher-order reflections from interfering with a wanted first-order reflection. But it was not until Bowman and his co-workers[29] pointed out, in 1966, that the silicon and germanium diodes, developed as gamma ray detectors, had acquired a sufficiently good resolution to be used in X-ray spectrometry, that energy-dispersive spectrometry (EDS) became viable. The resolution quoted in their paper is 1,100 eV but already a standard manufacturer's guarantee will be for less than 150 eV.

Germanium has a higher absorption than silicon, and is the favored detector for energies above 100 keV,[30] but in the normal X-ray analysis region silicon has adequate absorption and has other advantages. The chief of these is the relative stability of the finished detector at room temperature. Figure 2 shows schematically the nature of the device. The entering X-ray quantum produces ionization in the form of electron-hole pairs, and thus creates a charge, which is proportional to the energy of the original quantum. This charge is then swept out by the applied potential and a pulse is created in the preamplifier. Impurities in the so-called intrinsic region between the p- and n-type layers (the device is sometimes called a PIN diode) can result in leakage current and trapping centers with consequent noise and loss of resolution. The controlled diffusion of lithium atoms

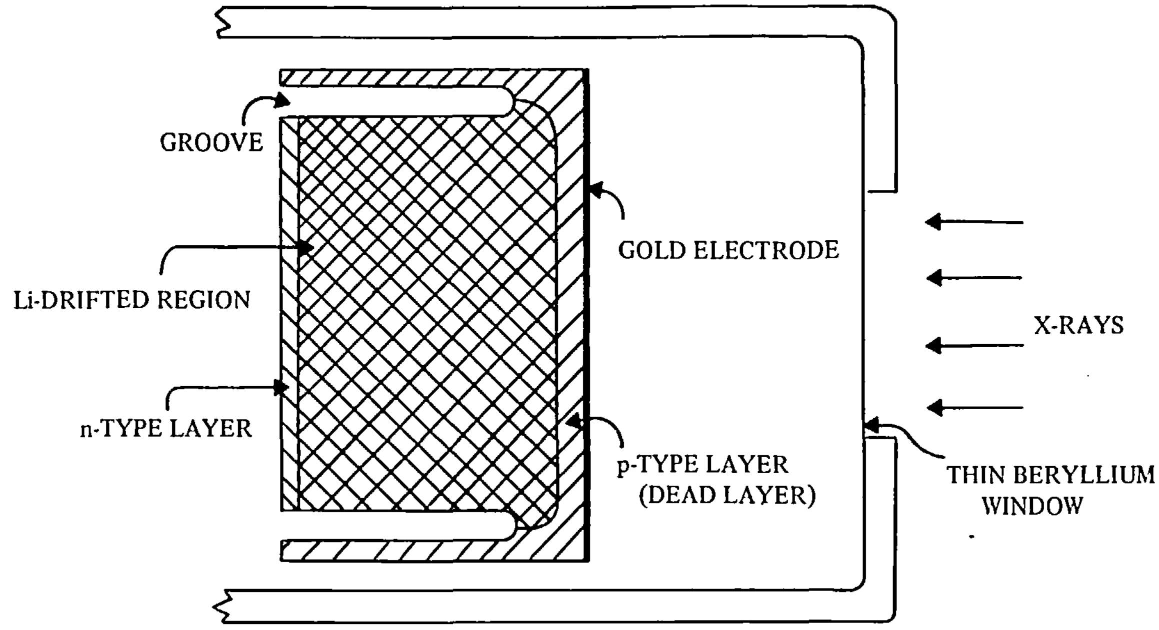

FIGURE 2. Schematic diagram of a semiconductor X-ray detector.

into this region cancels these effects, but at room temperature the lithium atoms remain mobile and it is necessary to maintain the detector at low temperatures. With no bias voltage applied, silicon detectors can be allowed to reach room temperature several times for short periods without damage,[30] but this is not true for germanium. During operation it is necessary in any case to maintain the device and its preamplifier at liquid-nitrogen temperature (77°K) to reduce thermal noise to acceptable levels.

The resolution for a silicon detector is given in eV by

$$(\text{FWHM}) = \sqrt{(\text{FWHM})^2_{\text{noise}} + [2.35\sqrt{F\varepsilon E}]^2}$$

where

F = the Fano factor[31] ≅ 0.1
ε = energy to create an electron hole pair (= 3.9 eV for silicon at 77°K)
E = energy of the X-ray quantum

With a presently achievable noise level of about 60 eV this corresponds to a resolution of about 140 eV at 5.9 keV for MnKα. The Fano[31] factor is still not sufficiently well understood to be predictable, but it seems unlikely that resolutions better than 120 eV will be reached in the foreseeable future. Detectors with the very low resolution values just discussed are at present small, with an area of about 10 mm^2. Frankel and Aitken[32] deal with the problems of maintaining high resolution with larger detectors and show that there is a degradation of resolution by a factor of 2.5 as the area of the detector is increased to 500 mm^2, but that this is largely due to electronic noise and therefore inherently improvable. Since the collection efficiency is linearly related to area, resolution may be profitably traded off against sensitivity for some applications where the signal is particularly weak.

In general, however, the nature of the detector is such that it is both desirable and possible to have it very close to the sample. The count rate can then usually be made high enough with a small detector to allow the benefit of the higher resolution to be obtained. Since the solid angle intercepted follows an inverse square law, a 10 mm^2 detector at 1 cm from the sample will collect as efficiently from a point source as a 500 mm^2 one at 7 cm.

A feature related to detector size and resolution is discussed by Goulding et al.[33] They demonstrate that background is partially due to degradation of pulses in the peripheral region of the detector and display a guard-ring construction which can decrease the background by a factor as large as 40. Landis et al.[34] were also responsible for the now commonly accepted opto-electronic feedback arrangement shown in Figure 3. Succes-

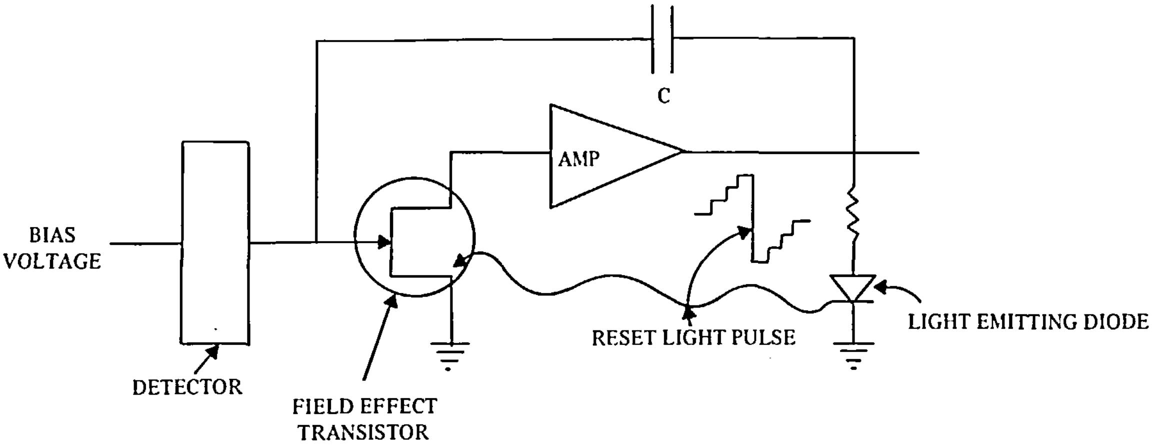

FIGURE 3. Opto-electronic feedback for an energy-dispersive spectrometer.

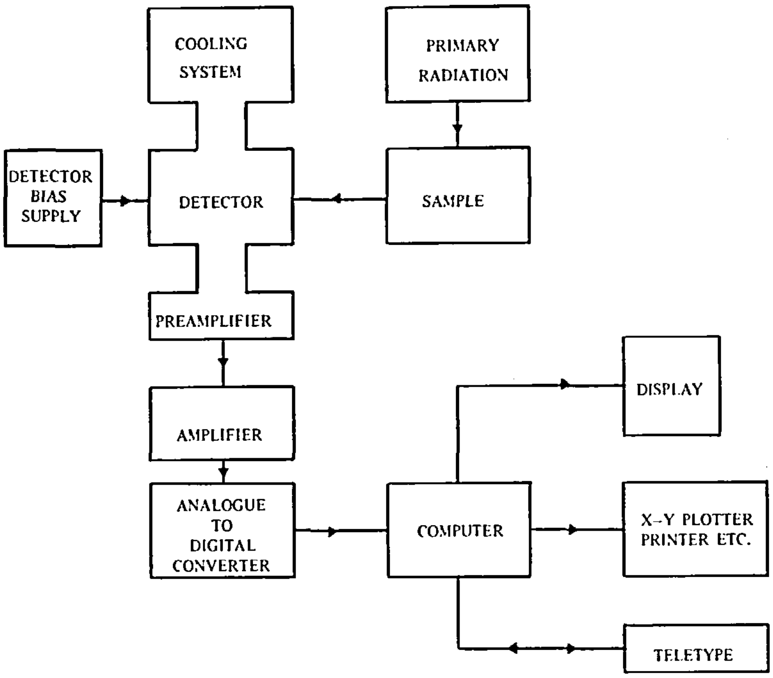

FIGURE 4. Block diagram for a typical energy-dispersive system.

sive pulses build up volts across a light-emitting diode until the latter is triggered, whereupon it shines light onto a photo-diode, discharging the voltage and resetting the system. This allows the input capacitance, and therefore the noise level, of the field-effect transistor (FET), which is used as a preamplifier, to be kept down without adversely affecting the performance at high count-rates. Resistance-coupled preamplifiers with low-noise capabilities are, however, still made.[35]

The main amplifier or pulse processor is complex and at present about 30,000 pulses/sec is the maximum that can be achieved without serious loss of resolution or linearity.[30] This is probably an even greater disadvantage relative to WDS than the resolution differences, because the whole spectrum and its background is included, and the count rate for the peak of immediate interest will always be very much smaller.

In the block diagram of Figure 4 it can be seen that the amplifier is followed by an analog-to-digital converter and traditionally by a hard-wired multichannel analyzer, but the latter is gradually being superseded by a minicomputer[36] with an inherent increase in flexibility. The same device can be used to collect, store, and process the data with a facility not open to wavelength-dispersive spectrometers.

One of the limiting factors of a semiconductor detector is its need for some protection, especially from the atmosphere. Because the surface of such a detector is cold, contaminants are rapidly deposited onto it. Protection from light and, when electron excitation is being used, from scattered electrons[37] is also necessary. The provision of suitable window material has improved to a stage where a 7.5-μm beryllium window is now standard. This has a transmission for NaKα radiation, at an energy of 1.04 keV, of about 60%.[38] Jones[39] has described a system whereby in clean, high-vacuum conditions the beryllium window can be rotated to leave the detector covered only by a 'thin vapor layer.' He shows spectra of oxygen and nitrogen Kα lines and Woldseth[30] has a spectrum of carbon Kα produced in a windowless system by proton excitation. The gold contact film and the dead layer (Figure 2) provide the ultimate barrier to even softer radiation.

III. EXCITATION

A. General

Up till now, most analysts have used X-ray fluorescence spectrometry, in which primary X-rays from an X-ray tube excite in the sample the secondary X-rays characteristic of the elements in it. This is because it has been, and will probably continue to be, the form of X-ray spectrometry with the soundest base and the widest applicability to inorganic quantitative elemental analysis.

Electron excitation was the earliest method used[2] and its modern reemergence under the title of Electron Probe Microanalysis[3] has led to its extensive use, but by metallurgists and geologists on the whole rather than by analytical chemists. This is because it was designed to offer analysis of the smallest possible volume (about 1 μm^3) and is, therefore, both expensive and less suitable for general analysis of massive samples. Electrons are, however, readily generated and manipulated, and some modern realities and future possibilities are discussed in detail below.

Mention has already been made (Section II B, C, and D) of portable spectrometers and these are almost, but not quite, all based on radioisotope excitation, which has been given a second wind by the emergence of EDS.[4,40]

As time has gone on fresh areas of analytical interest have emerged, environmental pollution being a recent notable example, and at the same time analytical instruments have become much more expensive. These two factors have probably combined to encourage the recent growth of interest in high-energy-particle excitation for characteristic X-rays. It shows promise for trace element analysis, but at a fairly high cost.

B. X-ray Tubes

Manufacturers have steadily increased the power of X-ray tubes and the stability of their generators to the present norms of 3 kW and 0.01%, respectively. The former ensures strong signals from the sample and the latter helps to facilitate high precision. Such tubes are usually evacuated and sealed to offer high energy-conversion efficiency, stability, and long life. No X-ray tube target is ideal over the whole analytical wavelength range but Ag, Rh, or Mo tend to be used as the best compromises. For the short-wavelength (heavier element) end of the spectrum W, Au, or Pt are the most suitable while for the light-element (F to Ca) end Cr has hitherto been the best. This has been partly determined by window thickness, because the thinner the beryllium window the higher the intensity of low-energy radiation emitted. Thinner windows, however, are now being fabricated for the heavier-element targets and the choice is no longer so clear cut.

The tubes just mentioned are designed for WDS work and are unnecessarily powerful for direct EDS use because of the counting-rate limitations already discussed (Section II F). Porter,[41] however, reviving the suggestion of Birks et al.,[338] points out that the use of secondary radiators, which can be changed at will, has the particular advantages that more efficient fluorescence and lowered background can be obtained. The former is arranged by choosing the secondary radiator to have its emission at energies just above the absorption edge of the element being sought. Several examples are given including the determination of lead in aqueous solution at the 10 ppm level with a statistical error of 5%.

The other approach is to use X-ray tubes of lower power and this line has been followed by a number of workers recently.[42-44] Dyer et al.[43] use a fairly conventional tube but with currents of the order of microamperes rather than milliamperes. Jaklevic and his co-workers[44] successfully reduce bremsstrahlung background by making a transmission tube with the output being drawn from the opposite side of the thin target to the electron beam. They have also designed a tube having a lower output but an even better signal-to-noise ratio using, as did Porter,[41] a secondary radiator but this time inside the X-ray tube. Yet another tube type is offered by McCrary and Van Vorous[42] as a potential replacement for a radioisotope source, namely a field emission tube. They and other authors point out that an X-ray tube can be turned off and is, therefore, safer in some ways than a radioisotope source.

The part played by the X-ray tube window in absorbing the long-wavelength radiation and reducing the efficiency of secondary X-ray production from the very light elements (Li to F) resulted in the pioneer work of Henke[45] with ultrathin-window tubes.[46] Schoenfeldt and Pluchery[54] have used a Henke-type tube, in a compact arrangement with a hexagonal sample holder and proportional counter detector, for elements as light as beryllium. Others[47,48] in turn removed the window completely, but poor stability, low yield, and other factors to be discussed later (Section VIII) have caused these devices to fail to achieve popular acclaim.

A recent attempt by Sahores and co-workers[49] to achieve similar ends differs in being, in reality, an electron excitation source with consequent advantages and disadvantages. It is a windowless 'X-ray tube' with a tungsten target operating on the cold-cathode gas-discharge principle. The vacuum, at somewhat less than 0.1 torr, is the normal one for an X-ray fluorescence spectrometer but there is automatic pressure regulation and gain control to provide stability. It is, however, the high yield of back-scattered electrons from the tungsten target that provides the X-ray excitation of the sample and other such devices are included in the next section.

C. Electron Sources

Electron sources have always been the most easily attained and most flexible for characteristic X-ray production but they have a number of disadvantages. They require the sample to be in vacuum and in most cases to have a conducting surface. The generation of X-rays is largely confined, for the energies commonly employed, to the surface layer about a micron deep, and so surface finish and homogeneity requirements are very restricted. Finally the production of bremsstrahlung or continuous background means a poorer signal-to-noise ratio than for X-ray excitation.

On the other hand, many, if not most, X-ray spectrometric samples are now subjected to vacuum anyway, matrix effects are reduced by the shallow penetration of the electron beam, radiations of the very light elements are more efficiently excited, and the much higher signals to some extent compensate for the higher noise levels.

A few commercial instruments exist in which an electron source covering an area of sample more than a square centimeter is used either alone[50,339] or as an alternative to a conventional X-ray tube.[49] These are capable of generating X-rays from any solid sample but are in the main designed for the lighter elements (F to Ca). The boundary line above which the sealed X-ray tube is more efficient lies in the region of silicon according to Strasheim and Brandt,[51] and also to Sahores et al.[49]

Until recently, electron sources covering less than a square centimeter have tended to be electron probe microanalyzers. These are expensive but the cost has lain in the complex electron optical and sample handling system to a greater extent than in the X-ray spectrometer itself. Not long after the energy-dispersive spectrometer was developed,[29] it found an ideal mate in the Scanning Electron Microscope (SEM). The large solid angle of collection of the EDS meant a statistically meaningful X-ray signal from a sample irradiated with a beam of 10^{-10} to 10^{-12} A, the current range required for high resolution SEM work. Recently the cost and complexity of some SEMs have been considerably reduced and the flexibility of EDS systems has increased, giving promise for the future.

A number of authors[51-53] have considered in very practical terms the comparison between fluorescent and electron-excited X-ray spectrometry. Foersterling et al.[53] tend to come down on the side of the electrons because of the light-element possibilities and the simpler relationship between intensity and concentration, but they agree that sample preparation is more difficult.

TABLE 2

Some Commonly Used Radioisotope Sources

Source	Half-life (yr)	Useful radiation	Energy (keV)	Highest atomic number elements usefully excited (K-radiation)
Bremsstrahlung				
Tritium	12.3		Up to 18.6	30 Zn
Promethium-147	2.6		Up to 225	60 Nd
X- and gamma-ray				
Iron-55	2.7	MnK	5.9	24 Cr
Cadmium-109	1.3	AgK	22	43 Tc
		γ	88	
Americium-241	458	NpL	11–22	69 Tm
		γ	26 and 59.6	
Gadolinium-153	0.67	EuK	42	88 Ra
		γ	97 and 103	
Cobalt-57	0.74	FeK	6.4	98 Cf
		γ	14, 122, and 136	

Colle and co-workers[55] have achieved some success in overcoming the disadvantages of electron excitation and retaining the advantages by the use of electrons with energies of several MeV. The sample surface becomes less important and empirically determined factors enabled three National Bureau of Standards metal alloys to be analyzed with fair accuracy even for constituents down to 0.06%.

D. Radioisotope Sources

The possibility of using a radioisotope source to excite X-rays was mooted as early as 1946.[56] Twenty years later Rhodes,[40] one of the pioneers in this field, was able to write that radioisotope X-ray analysis was in a phase of rapid development. At that time EDS was still nonexistent, and even a conference in 1970 devoted to applications of low-energy X- and gamma rays[57] contained only three papers[58-60] discussing the use of semiconductor X-ray detectors. Two years later, however, a fresh review by Rhodes[4] listed 47 papers on semiconductor spectrometers as opposed to 20 with other detectors.

The major advantage of the radioisotope source is its small size and lack of peripheral equipment. But its use requires a sacrifice in intensity relative to an X-ray tube of about 10^6 to 10^7 times.[61] A less serious disadvantage is that although there is a very wide range of sources to chose from (Table 2), it is even more difficult than with X-ray tubes to find a really suitable source to cover a broad enough X-ray spectral band. Sources can offer α-, β-, γ-, or X-radiations, but α-sources, which would have some advantages (Section III E), are highly toxic and difficult to manufacture as sealed sources with sufficiently thin but radiation-resistant windows.[61] Franzgrote,[62] however, was able to use a curium-244 source with two 1,200-Å-thick aluminum oxide windows, and with a silicon detector. He found that X-ray spectrometry complemented the alpha-scattering method for rock analysis and improved on it, for instance, in the determination of potassium and calcium. He suggested it as an addition to the equipment proposed for on-the-spot analysis of the Martian surface. By themselves, β-ray emitters provide bremsstrahlung radiation, i.e., the disadvantages of electron excitation (poor signal-to-noise ratio) without the advantages, but tritium mixed with zirconium or titanium, for example, will give characteristic X-rays of the 'target' material and provide a spectrum more nearly allied to the output from an X-ray tube. Promethium with aluminum or a suitable ceramic is another such pair of possibilities. Efficiency for these is low, however, and direct X- or gamma-ray sources have advantages. Americium-241 (Table 2) is probably the most broadly useful source[30] for overall efficiency of excitation and it has a suitably long halflife.

E. High-energy-particle Excitation

Chadwick[63] in 1912 demonstrated that characteristic X-rays can be generated by α-particle bombardment, but it was not until some very

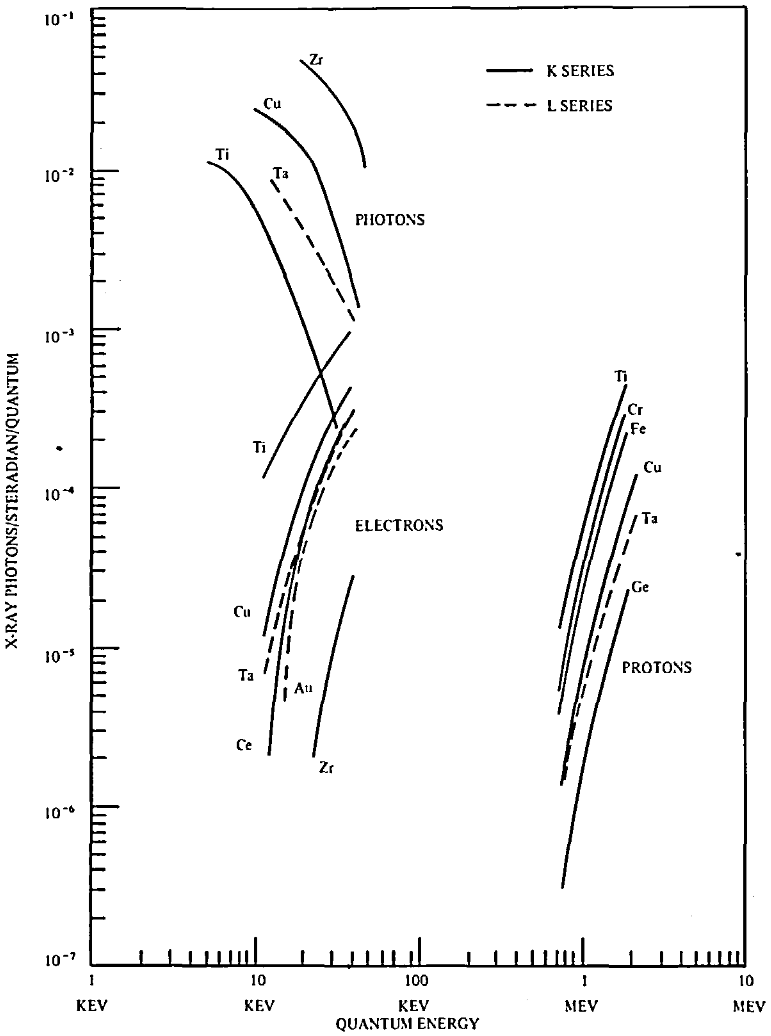

FIGURE 5. Number of X-ray photons emitted from a bulk specimen as a function of the energy of the exciting quanta. (From Birks, L. S., Seebold, R. E., Batts, A. P., and Grosso, J. S., *J. Appl. Phys.*, 35(9), 2578, 1964. With permission.)

practical work in 1964 by Birks et al.[64] that general interest in high-energy particle excitation for X-ray spectrometric analysis became aroused. They pointed out that whereas the efficiency of X-ray production for a given element decreased with increasing primary photon energy, the opposite was true for particle excitation. Also, for particles of a given energy the efficiency of characteristic X-ray production increased as the atomic number decreased. This, of course, is one reason why it has been found preferable to use electrons in some cases for the lighter elements as discussed earlier (Section III C, and References 49, 51, 52, and 53). Figure 5 shows some practical comparisons. The new point, however, made by Birks et al.[64] was that protons, unlike electrons, do not interact inelastically to any extent with the atoms in the sample and so the background is very low, and possibilities for trace analysis are enhanced. They finish, however, by indicating the need for a low-cost proton source, and the lack of emergence of such a source is one reason for continuing uncertainty as to future progress in this field.

There are, however, enough high-energy particle generators in existence to have produced a steady flow of developing information in the last few years. Protons are still the most popular excitors and likely to remain so because of the relatively moderate energies required (0.1 to 10 MeV). Kamada et al.[65] worked at 0.2 MeV and used WDS, achieving detection limits of 14 and 90 ppm

For boron and carbon, respectively. Johansson, Akselsson, and Johansson,[66] working at 2.5 MeV, have clearly demonstrated detection limits of around 10^{-12} g. The concentration limits associated with this weight are less clear, but at least 0.1 ppm seems possible without preconcentration. Duggan and co-workers[67] also indicate an experimentally confirmed limit of 10^{-12} g. In both sets of work the sample is in the form of a thin foil or sheet unsupported or on carbon, aluminum, or plastic. With very low levels of detection, impurities in the backing foil become important and ultrapure carbon is used by Duggan et al.[67] Umbarger et al.[68] compare the detectability limits with Mylar foil backing of 0.00015 and 0.00025 in. thickness and with 1-3 MeV protons. In the former case the thinner foil gives an advantage of approximately four times, while the limit improves roughly linearly with energy. All the above work, with the exception of Kamada's, was carried out with an EDS system and it is one of the main points in Johansson's[66] argument that many elements can be determined simultaneously with a sensitivity not matched by many other techniques. Duggan et al.[67] go further and suggest that this method of analysis is potentially an order more sensitive than neutron activation. They do not, however, give practical examples to substantiate the claim. The limitations of a silicon detector are dealt with in this context by Verba et al.[69] and they propose a system with two energy-dispersive detectors and 24 crystal monochromators.

A proton probe with a resolution of about 10 μm was used by Poole and Shaw,[70] who achieved a 10-ppm limit of detection with it.

Comparison between proton and alpha-particle excitation is made in the 1-12 MeV region by McCoy and colleagues[71] who propose the technique especially for studying the depth of surface contamination by varying the ion type and accelerating potential. Alpha particles require somewhat higher energies than protons for the same X-ray cross section but produce theoretically even less bremsstrahlung background. Watson et al.[72] used a 50-MeV alpha-particle beam and achieved sensitivities varying from 50 ppm for titanium to 130 ppm for elements above tin in atomic number. Comparison of Mylar, Kapton®, and Teflon® as backing films for samples to be excited by alpha particles was carried out by Flocchini and others.[73]

Even heavier ions are proposed by some workers.[74-76] Saltmarsh et al.[75] in particular used 20-MeV oxygen ions to study the diffusion of La_2O_3 along NaCl crystal surfaces. They had to use an absorber, Mylar in this instance, to reduce the sodium and chlorine radiation reaching the silicon detector. Shabason and colleagues[76] also used an absorber to keep down the count rate due to light-element impurities. Their use of 40-MeV oxygen ions, for which the range in carbon is only 200 μm (as against 1,200 μm for 4 MeV protons), allowed them to use solid samples, in such a way that X-ray absorption was small enough to ignore in most cases. Calibration curves were obtained by mixing known small weights (1,000–4,000 ppm) of chosen elements with a binder such as Li_2CO_3 and pressing into pellets. From these 'efficiency' curves for E versus atomic number where

$$E = \text{counts/nC} \times f$$

and f is the fractional weight, were used directly to provide absolute abundances for impurities in beryllium, aluminum, and coal-ash. Detection limits down to about 10 ppm were achieved, but with a detector of only 250-eV resolution the coal-ash gave problems due to the large number of elements present and, therefore, the numbers of overlapping lines.

It should be noted that apart from the relatively early (1969) work of Kamada[65] and the proposals of Verba,[69] all the investigators mentioned in this section used energy-dispersive detectors (even Birks[64] used the energy dispersion of a proportional counter in 1964). Even for those with particle sources readily available it seems likely that progress would have been slower but for the advent of EDS.

IV. X-RAY SPECTROMETRIC EQUIPMENT

A. X-ray Fluorescence Spectrometers

1. Conventional

a. **General** – The medium to large conventional X-ray fluorescence spectrometers fall into three categories:

1. Sequential: flat-crystal optics[77]
2. Simultaneous: flat-crystal optics[78]
3. Simultaneous: curved-crystal optics[79]

The first type is the simplest and most widely used, and although no startling developments have taken place recently, there has been a steady improvement by manufacturers in the quality and range of crystals available, in the transmission of the collimators, the stability and power of the X-ray generators, and the reliability and versatility of the electronics. The stepping motor allowing preselection of a number of set angles, and hence wavelengths, has meant the retention of flexibility but with an increase in automation and reduction of operator error, albeit with some increase in cost. For most spectrometers in this class fluorine can now be included[80] where magnesium used to be the lightest element in the range. One commercial instrument allows sample excitation by either a conventional X-ray tube or a Sahores[49] type (Section II B) with only electrical changeover and so includes elements down to boron.

The simultaneous spectrometers are inherently complex, expensive, and relatively inflexible instruments. They allow as many as 24 different wavelengths to be monitored at the same time with an individual crystal and detector for each channel. This allows the optimum crystal and detector to be chosen for the determination of each element, but makes any change likely to be difficult and time-consuming. Although the types of crystal that can be shaped are limited, the increase in collection efficiency makes the curved-crystal spectrometer rather more popular in simultaneous spectrometers especially if the crystal shape permits large aperture collection.[79] This type of spectrometer is ideal for process control in, say, large steel or cement works where the need is for speed and precision rather than flexibility.

At the other end of the scale McCrary and Edmonds[81] describe a portable instrument with a battery-powered X-ray tube,[42] dual scintillation counters, and balanced filters weighing only 5.5 kg. It is intended for single-element analysis and has a quoted sensitivity of 100 μg/cm^2 for copper.

b. **Automation and computer control** – Predictably, the field of computer control and data handling has advanced for X-ray spectrometry as for many other instrumental analytical techniques. Initially automation was carried out by mechanical and hard-wired peg board methods. Choice of tube voltage and current, collimator, crystal, detector, and counting time for a particular X-ray emission wavelength could all be made beforehand, and a series of samples analyzed for a number of elements without further attention.[82,84,91] However, as minicomputers have become cheaper, more use has been made of them both for control[85-87] and for data processing.[78,88] Rasberry[86] surveys the position (including electron-probe instruments) and points out that in some cases computers have been used without any specific purpose in mind and that this is liable to lead to loss of efficiency and flexibility.

Croke and Jenkins[89] describe a combination in which a stepping motor programmer provides flexible control of angles with 64 programmable positions and a microcomputer (Olivetti® P-602) can collect the data and process it with simple calibration corrections. With a multichannel instrument for which control is not required[90] and a slightly larger (8K) computer Jenkins[78] deals with rather more sophisticated sample- and data-handling as applied particularly to high alloy steel-making control. Enz[83] describes a system for foundry control where the whole process, from sample preparation to analysis print out, is automatic and takes about 5 min.

2. *Milliprobes*

Only a few authors[92-94] have been motivated in recent years to make[94] or to use[92,93] an X-ray fluorescence spectrometer in which the area of sample irradiated is small. The instrument of Campbell et al.[94] has a spatial resolution of 0.3 mm and was designed to be able to scan over relatively large samples for local variations, without having to have a conducting surface or be in high vacuum. For most purposes, however, the electron probe has been so successful that X-ray milliprobes are inefficient by contrast.

3. *Energy-dispersive Instruments*

a. **General** – Energy-dispersive systems for X-ray fluorescence spectrometry offer so many new possibilities and are proliferating so rapidly that it is worth reiterating their disadvantages before these are forgotten. Resolution is an order of magnitude poorer than for crystal spectrometers so that, for example, SKα (2.31 keV), MoLα (2.29 keV), and PbMα (2.35 keV) are virtually indistinguishable; signal-to-noise ratio is less because the signal information is spread over a wider energy band, and hence detectable concentration limits cannot be so low,[95] and count rates – for the whole spectrum – are at present limited to something over 10^4 counts/sec. The last introduces a statistical limitation on achievable precision, but conversely EDS systems are so stable that counting times can be relatively long. Again, some of the disadvantages of line overlap, because of inadequate resolution, can be overcome by spec-

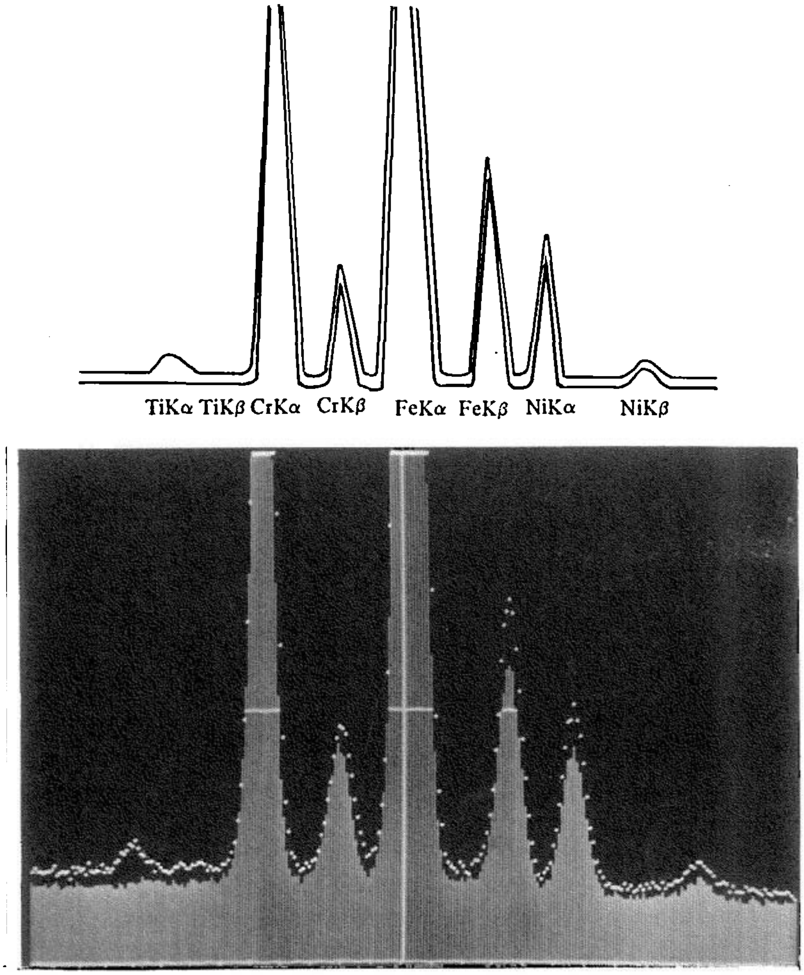

FIGURE 6. Energy-dispersed spectra from stainless steel samples with and without 0.4% titanium.

trum-stripping techniques. The peak shapes are nearly gaussian and can be produced artificially, if necessary, or better still by use of a suitable sample and then 'stripped' from the spectrum of the unknown to reveal the hidden peaks.

The advantages are dealt with by a number of authors[96–98] in different contexts, advantages which have required also the development of the low-cost minicomputer before they could be fully realized. The more obvious points in favor of EDS are

1. Very rapid qualitative analysis over the whole periodic table except $_{1}$H to $_{10}$F.
2. The spectra are very simple, with no higher orders.
3. Rapid fingerprint identification of materials by comparison with stored spectra (see Figure 6).
4. Lower-power X-ray sources can be used.
5. Less expensive altogether because less complex than WDS.
6. Data processor already inherently available.
7. Versatile information presentation possible.
8. All-solid-state circuitry offering stability and reliability.

b. X-ray tube excitation – Russ[97,99] goes into detail about spectrum-manipulation possibilities and discusses accuracy and precision. Wood[96] describes an instrument with an air-cooled 250-W X-ray tube and details the facilities available on a push-button console. A more complex system is dealt with by Martin and Klein[100] in which both elemental and compound analysis are performed simultaneously. Two diffraction angles are used to provide spectra in which the fluorescent lines will not have moved but the diffraction lines will. Carr-Brion[98] is enthusiastic about the possibilities of EDS arrangements for on-stream analysis. He points out the greater ease of determining, in air, elements as light as aluminum, because of the close approach of the detector to the sample. He claims that the restriction on sample surface position is reduced from ± 50 μm to ± 250 μm with reduction of mechanical cost and suggests that the tube power may be as low as 0.1 W. Feasibility studies were carried out on a wide range of slurries, ores, and sinters with gratifying success.

X-ray tubes specifically used[41] or designed[42-44] for EDS have already been mentioned in Section III B.

c. Radioisotope EDS – At first sight the stability and simplicity of radioisotope sources combined with the present lack of a requirement for high intensity with a semiconductor detector would suggest that the marriage of the two would be ideal, and yet only a few instruments of this type appear to have been designed. Rhodes[4] in a recent review, having expressed surprise at the sluggishness of the portable-analyzer market, gives at least part of the answer in pointing out, that if an instrument cannot be independent of power and other supplies, the motivation to use radioisotope sources is reduced. The other main reasons, clearly delineated by Woldseth[30] lie sometimes still with too low intensity but more often with limited efficient (high signal-to-noise level) range. The latter is of course true also for X-ray tubes but the inherent high intensity of the latter allows a flexibility in choosing filters or secondary radiators[41] less open to radioisotope sources.

Nevertheless, a number of useful instruments have been developed[102-108] and Figure 7 shows typical geometries. One of the earliest by Yamamoto[108] had a detector resolution of only 512 eV, but with an iodine-125 source he was able to detect as little as 35 ng of molybdenum. More up-to-date work by Ehn[105] with the same source, as well as with the more popular americium-241, was designed for the determination of silver in photographic materials. It is unusual in that, in contrast to the geometry of Figure 7, the sample is between the point source and the detector, while lead is used to stop direct irradiation of the source. The advantage is that the position of the film under test is much less critical. The instrument of Rhodes[59] is also designed for thin films but the source-to-specimen distance is arranged for maximum count rate and can tolerate a millimeter change in position. Gehrke et al.[102] were concerned with low-level detection of iron in oil and compared nine radioisotope sources for this purpose. They achieved a sensitivity of a few ppm with germanium-71 but regretted its short half-life of 11 days. One of the few portable instruments (≤20 lb) was designed by Laurer and coworkers[103] specifically to check for lead in paint. They used cadmium-109 and a germanium detector to measure the lead K rays *in situ* from paint surfaces.

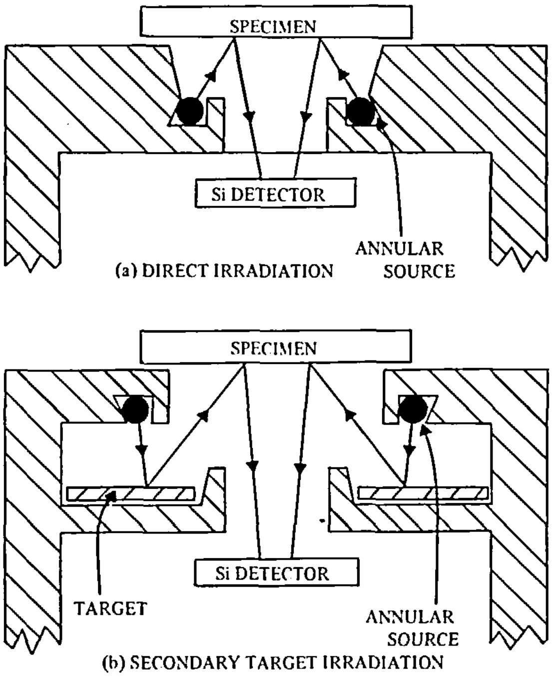

FIGURE 7. Schematic diagram of two possible annular radioisotope-source energy-dispersive-detector arrangements.

The above instruments were mostly intended for single-element applications, but Harrison and Kenna[106] used a system for fingerprinting alloys, and Hurley et al.[107] dealt with anything from rocks to paintings. They used an americium-241 source with secondary target which could be varied to suit the occasion. They recommend the choice of a target to provide its peak back-scatter well above the energy of interest.

Some interesting work which almost evades classification was done by Mantel and Amiel.[101] Their samples were subjected to neutron irradiation but were then measured for X- rather than gamma radiation. Thirty elements were studied and a number of practical examples were given.

B. Electron-beam Instruments

1. Electron-beam Instruments with WDS

Since the invention of the linear spectrometer[109] and the application of multilayer stearate crystals[110] to light-element analysis there have not been any startling changes in wavelength-dispersive spectrometry for electron probe microanalysis. A host of developments in the uses and variety of electron-beam instruments have taken place[111] but few of them have added much to the X-ray analysis facilities. New 'brighter' electron sources[112] now allow better resolution or higher X-ray count rates and the combination of electron microscopy with X-ray spectrometry has been skillfully achieved[113] to permit detection limits down to 10^{-18} g.[114] This compares well with the 10^{-12} g achieved with proton excitation[66,67] but represents a concentration sensitivity of only 0.01%.[115] The technique of elemental mapping – displaying variations in the concentration of a chosen element over an area of surface – is a possibility not available with other X-ray sources and some recent improvements have been achieved.[116,117,123]

The minicomputer is again responsible for the most notable developments in electron-probe instruments, and automation[86,119-128] has been undertaken by many workers. As an extension of the normal use of a computer Thresh and Keller[128] have a procedure for dealing with data from 300 points. On the other hand, Jeffries and Long,[119] Lifshin,[125] and Finger and Hadidiacos[127] control spectrometers for multielemental analysis. Kunz and Eichen[124] describe a method for computerized peak location in as little as 10 sec arising from their much more general control system[121] covering specimen and electron-beam positioning as well as full spectrometer control, data processing and reporting. Colby[126] has gone further still and included electron gun and lens automation, and vacuum-system and detector-voltage control.

Gavrilovic,[122] in a rather novel application, uses a computer to seek out particles with a predetermined composition. An air-pollution sample, for example, had 50 ppm of lead in it and an automated search found 15 lead-containing particles in 48 hr.

Electron-beam instruments covering relatively large sample areas (say 1 cm^2 or more) have already been mentioned[49,50,339] in Section III C.

2. Electron-beam Instruments with EDS

a. Conventional electron probes – Little or no instrumental development was necessary to permit the marriage of electron-probe microanalyzers and energy-dispersive spectrometers. The potential for rapid qualitative analysis was soon realized and was inevitably followed by a steady stream of papers dealing with quantitative possibilities.[131-135] This aspect will be enlarged upon later but has not led to any specifically instrumental changes, other than the suggestion that single-channel analyzers have count-rate advantages.[132,134]

b. Scanning electron microscopes – The scanning electron microscope (SEM) as a commercial instrument is not much older than the high-resolution semiconductor detector, and the two in harness are providing a minor revolution in X-ray spectrometric techniques. The SEM was developed to throw off the shackles of the very restricted depth of focus and limited resolution of the optical microscope while avoiding the difficult sample preparation necessary for the transmission electron microscope. Because the electron-beam currents were three or four orders of magnitude smaller than in electron-probe microanalyzers, only a few hardy spirits ventured to attempt to collect the X-ray quanta automatically generated and to use them for analysis. In any case the rough samples for which the SEM was designed – and used – were completely unsuitable for WDS. But the energy-dispersive spectrometer altered the situation completely because it not only permitted the simultaneous detection of all of the elements, but also increased the solid angle of interception of the X-ray beam from 0.0001 sr to at least 0.01 sr[118] ($\geqslant$0.1 sr can now readily be achieved) so that sensitivity was on a par with the conventional electron probe instruments. The large solid angle also meant that a fair degree of specimen roughness could be tolerated for qualitative and even semiquantitative analysis.

The analyst has therefore, been presented with a tool, rapidly becoming relatively cheaper (both the scanning microscope and the minicomputer), which allows him to examine a metallic sample within 2 min and a nonmetallic sample within 10 min, after evaporation of a thin film, usually of carbon, onto it. The examination, at magnifications from 10 to 20,000 times, allows him to choose any area from 1 cm^2 to less than 1 μm^2 and, within seconds, to obtain a spectrum that, with very few uncertainties, can be interpreted to reveal all elements with atomic number higher than 10, which are present to more than 1% of the volume (~ 1 μm deep) examined. This is in no way competitive with the normal X-ray fluorescence equipment, but it adds a new dimension to identification analysis.

Once again, as soon as it had been realized that the two instruments, SEM and EDS, were compatible, very little instrumental development was required. Because the specimen-handling requirements of the SEM are more flexible than those of the electron probe, it became easier to get the detector above and close to the sample.[118]

The work of Russ[129] is typical of several successful essays into the application of EDS to the transmission electron microscope; he talks about detection of 10^{-18} g or 100 ppm with a spatial resolution of a few tens of nanometers.

V. QUANTITATIVE X-RAY SPECTROMETRY

A. Electron Excitation (WDS)

For a brief period after the invention of electron-probe microanalysis by Castaing[3] there was a hope that a virtually absolute instrumental method of analysis had been devised. All that was required was a ratio of the X-ray intensity obtained from the desired element in the sample to that obtained from the pure element. This ratio was the sought-for weight fraction. Such simplicity was not to be, however, and the years between have called forth tremendous efforts from many scientists towards the efficient and accurate conversion of X-ray intensities into concentrations. Nevertheless, this aspect is being reviewed before that of allied work in the X-ray fluorescence field, because there has recently been some convergence. Electron-probe correction procedures are based on a reasonable degree of understanding of the processes involved and, with only pure-element standards, have for some time offered a relative accuracy of ± 2%, at least within the range of atomic numbers from 11 to 30.[136] As will be seen in the next section, X-ray fluorescence users, having proved the reliability (to 0.1% relative) of methods employing closely matching standards, are trying to emulate the electron-probe workers and dispense with standards as far as possible.

The now popularly termed 'ZAF' approach is almost universally applied to the conversion from X-ray intensities to concentrations, with the minimum number of standards. The appellation ZAF arises from the three main corrections, atomic number, absorption, and fluorescence. A fourth correction for the effect of the continuum has rarely been applied, both because its application is difficult and because its effect is relatively small, but some recent work by Springer[137] may lead to its more frequent addition in the future.

So much has been published about ZAF and other correction procedures that this is a difficult field to cover, but two valiant attempts at collection and collation of work, those of Martin and Poole[138] in 1971 and Beaman and Isasi in 1970,[139] can offer a useful starting point. In fact, as indicated by Reed,[136] no really major advances have taken place since then. Martin and Poole[138] list a formidable array of attempts, theoretical and practical, to find a calculable relationship between measured X-ray intensities and the concentration of the element being studied. They show clearly the similarities and differences between the methods and are able, to some extent, to check their comparative success. Beaman and Isasi[139] list 40 computer programs for the calculation of element concentrations and give a detailed comparison of the models chosen by the programmers and the strengths and weaknesses that they found. Since it is impossible here to repeat these two compilations, a somewhat arbitrary selection from the formulae offered has been made with apparent popularity and success in mind. There are, however, many other approaches that have been and are still being successfully used.

The equation number 1 that follows shows the typical ZAF type of corrections to the measured intensities.

$$C_A = \frac{I_A}{I_{(A)}} \cdot \frac{R_{(A)}}{S_{(A)}} \cdot \frac{\Sigma C_i S_i}{\Sigma C_i R_i} \cdot \frac{f(\chi)_{(A)}}{f(\chi)_A} \cdot \frac{1}{1 + \Sigma I_{Fi}/I_A} \tag{1}$$

R; experimentally determined values by Bishop

$$S = \text{const.} \frac{Z}{A} \cdot \frac{1}{E} \cdot \ln\left(\frac{E}{J}\sqrt{\frac{2.718}{2}}\right) \tag{2}$$

$$E = (E_o + E_c)/2 \tag{3}$$

$$J/Z = 14.0\,[1 - \exp(-0.1Z)] + 75.5/Z^{Z/7.5} - Z/(100 + Z) \qquad (4)$$

$$f(\chi) = \frac{1 + h}{(1 + \frac{\chi}{\sigma})\,[\,1 + h\,(\,1 + \frac{\chi}{\sigma})]} \qquad (5)$$

$$h = 1.2\,A/Z^2 \qquad (6)$$

$$\chi = \mu \operatorname{cosec} \theta \qquad (7)$$

$$\sigma_H = \frac{4.5 \times 10^5}{E_o^{1.65} - E_c^{1.65}} \qquad (8)$$

$$\frac{I_{FB}}{I_A} = 0.5\,P_{ij}\,C_B\,\frac{r_{A-1}}{r_A}\,\omega\,(B)\,\frac{A_A}{A_B}\left(\frac{U_{OB} - 1}{U_{OA} - 1}\right)^{1.67}\frac{\mu_{(S)B}}{\mu_{SB}}\left[\frac{\ln(1 + u)}{u} + \frac{\ln(1 + v)}{v}\right] \qquad (9)$$

$$P_{ij} = k_i/k_j \quad P_{KK} = P_{LL} = 1,\ P_{KL} = 0.24,\ P_{LK} = 4.2 \qquad (10)$$

$$(B) = \text{a numerical constant} \qquad (11)$$

$$U_o = E_o/E_c \qquad (12)$$

$$u = \mu_{SA} \operatorname{cosec} \theta/\mu_{SB} \qquad (13)$$

$$v = \sigma/\mu_{SA} \qquad (14)$$

$$C_2 = \frac{k_2\,C_1\,(1 - k_1)}{k_2\,(c_1 - k_1) + k_1\,(1 - C_1)} \qquad (15)$$

Subscript A: refers to element A in the sample
Subscript (A): refers to element A in the standard
Subscript B: refers to element B in the sample
Subscript S: refers to the sample
Subscript (S): refers to the standard
Subscript i: refers to element i in the sample
Subscript F_i: refers to fluorescent radiation from element A caused by element i in the sample.

A_i = atomic weight of element i
C_i = weight fraction of element i in the sample
I_A = measured X-ray intensity from element A in the sample
$I_{(A)}$ = measured X-ray intensity from element A in the standard
I_{F_i} = calculated X-ray intensity from element A due to characteristic fluorescence by element i
R = fraction of incident electrons absorbed
S = stopping power of the target for incident electrons
Z = atomic number
E_o = energy of the incident electrons
E_c = critical excitation energy for radiation from element A
χ = μ cosec θ
μ_{XY} = mass absorption coefficient of matrix X for characteristic radiation from element Y
θ = X-ray take off angle
r_A = ratio of absorption coefficients on either side of absorption edge for A
σ_H = Lenard coefficient as modified by Heinrich
ω = X-ray fluorescence yield
k = ratio of X-ray intensities, sample/standard.

The first ratio is that of measured intensities, in this case as commonly, with the denominator obtained from a standard containing only the element being determined. It is assumed that these intensities have already been corrected (or will be corrected by the computer program), at least for background and dead time. Checks for drift and other errors outside the expected statistical range can also be included. Hooton and Parsons[140] have devised a new method based on mean square successive difference to detect and distinguish between drift and oscillations.

The second and third ratios in Equation 1 deal with the so-called atomic number correction (Z) and the fourth with the absorption correction (A). This combination is due to Duncumb, Shields-Mason, and da Casa.[141] The atomic number correction is concerned with interaction between the electron beam and the sample. Both the stopping power (S) and the back-scattering (1-R) are markedly affected by the energy of the incident electrons and by the 'mean atomic number' of the sample. For the back-scattering factor Duncumb uses values determined experimentally by Bishop,[142] and for stopping power the

Bethe[143] Equation 2. The absorption correction, Equation 5, is a simplified form of Philibert's[144] equation. The symbol σ, due to Lenard,[145] is concerned with the number of electrons at a given depth and is given by Philibert as a function of E_0 only. Several modifications to the evaluation of σ have been made and the one now generally accepted as being satisfactory is that of Heinrich,[146] σ_H in Equation 8. Some recent work by Brown and Parobek[155] on X-ray production in depth for aluminum, copper, silver, and gold confirms the validity of Heinrich's proposal. The most popular fluorescence correction (the last term in Equation 1) appears to be that of Reed[147] and is given in Equation 9. The values for P_{KL} and P_{LK} are Reed's own values and (B) is given by Worthington and Tomlin.[148]

Because the right-hand side of Equation 1 contains the elemental concentrations, iteration procedures are necessary to complete the calculation. The hyperbolic method outlined by Criss and Birks[149] is carried out according to Equation 15, and used by Heinrich[150] in his program (COR). A more recent version (COR 2), by Henoc, Heinrich, and Myklebust[151] offers a very rigorous correction procedure with space for up to 15 elements at as many as 100 measurement points, and with many useful options. It includes the continuum fluorescence correction pioneered by Henoc,[152] but without the necessity for earlier approximations.[150]

Further discussion of the absorption correction by Heinrich, Gakowitz, and Vieth,[153] in which four different expressions were used, has demonstrated that wide variations are possible without serious error.

Uncertainties in the values of mass absorption coefficients are frequently given as a major source of error both in electron-probe[150] and X-ray fluorescence calculations. Preuss[154] has made one of the latest attacks on this subject using formulae based on work of Kelly and Heinrich, and Woodhouse et al.[168] have determined values in the 1 to 10 Å range for gold, lead, and bismuth. Preuss has also[156] studied the atomic number correction with particular reference to thin films. In the biological field in particular[158] they do not yield to the theoretical approach outlined above.

Monte Carlo methods, in which random electron-scattering paths are computer-calculated, were discussed by Archard and Mulvey[159] in 1963, and have since continued to receive somewhat desultory attention. Shimizu and fellow workers[160] propose the Monte Carlo technique for the now important case of an inclined target. In the use of an SEM the sample is usually inclined to the beam and this has hitherto proved difficult to cater for by classical correction procedures. Heinrich[161] makes the same point and, like Hall,[157] indicates thin films as another area of application.

Not surprisingly, correction procedures have been less effective with nonconducting samples, in the mineralogical field, for instance. One of the drawbacks is the evaporated conducting film required on the surface. Kerrick et al.[162] have studied the monitoring of carbon-film thickness and its effects on the absorption of electrons and X-rays.

A novel suggestion by Frazer, Fujita, and Fitzgerald[163] involves eliminating some of the empirical corrections by making measurements at more than one electron-beam energy and extrapolating to E_c, the excitation potential for the desired element. At this point all corrections other than stopping power become negligible, but because X-ray generation also falls to zero no measurements can be made at E_c itself. The authors point out that the energy of the electron beam at the sample must be more accurately known than is common.

The region of light elements and soft X-rays is yet another area where conventional correction procedures fail. The fact that absorption coefficients are very high and uncertain is one reason for this failure. Kyser and MacQueen[164] propose a gaussian curve for $f(\chi)$ and use experimentally determined absorption coefficients. Henke[165] in turn reviews theoretical work on low-energy interactions between electrons, X-rays, and solids, and describes methods used by himself for measuring such interactions.

B. X-ray Excitation (WDS)

1. General

For quantitative analysis, the advantages of X-ray over electron excitation are, that the sample need not have an electrically conducting surface and that the volume of sample irradiated is so much greater that heterogeneity is less important. Compared to many other analytical methods, however, the depth sampled is still small and for acceptable accuracy heterogeneity must be reduced below certain limits with special attention to the surface layer.[166] For powders, Claisse[167] was one of the first to study the problems of particle size and the effects of the presence of different phases. Others have followed his lead[169-171] and Berry[172] has derived theoretical formulae and shown that there is a reasonable match between theory and experiment for a number of different minerals. Rhodes and Hunter[173] have demonstrated that some simplification can be accepted for certain practical applications, such as the analysis of air pollutants collected in filters. Jenkins,[174] with a very simple model shows that when two widely different wavelengths (Kα and Lα, or Lα and Mα) can be used for the same element, particle-size effects can to some extent be predicted. For on-stream analysis[98] of ores and similar materials heterogeneity is often the most intractable problem.

With solid samples that are known to be, or have been prepared to be, inherently suitable, most quantitative X-ray fluorescence analysis is carried out with standards closely matching the samples in physical form and composition. This is where it can and does differ from electron-probe work. With this approach a large number of standards are required if a sample system of any complexity is to be catered for, but high precision can be achieved.

High accuracy is also possible but it is usually not long before 'matrix effects' begin to introduce errors. The general trend of such effects is readily predictable in most cases, but Mitchell and Kellam[175] among others have demonstrated that unexpected reversals can take place.

One simple method, proposed many years ago by Andermann and Kemp[176] for reducing errors due to variable matrices, is to take a ratio between the X-ray intensity from the element of interest and the intensity at a suitably chosen scattered background wavelength. Variations in the matrix affect both the wanted line and the background. This approach has undoubtedly had its successes[177,178] but is not universally applicable. Clark and Mitchell[179] agree with Taylor and Andermann[178] that a short and predominantly incoherently scattered wavelength is likely to be most suitable, and show that the system works for copper but less well for iron in their case.

Any scheme for quantitative analysis requires that the measurements of X-ray intensity should be adequate and Plummer[180] has revived and extended expressions to allow the optimum counting strategy to be followed. Currie[181] has dealt with a similar topic, namely the definitions of detection limits in terms of counting statistics and backgrounds. He defines clearly (1) the 'critical level' or decision limit for indicating whether or not detection is indicated, (2) a 'detection limit,' and (3) a 'determination limit' for a satisfactory quantitative estimate.

For most analysts, however, the restrictions and inadequacies of internal or closely matching standards eventually become intolerable and more general methods for obtaining accurate quantitative results with fewer standards are sought. Not unnaturally, attempts to follow electron-excitation procedures have been made but with almost opposite results. The use of fundamental parameters is much more difficult in the case of X-ray tube excitation because of the complex nature of the primary beam and because the depth within which the X-rays are generated is great enough to cause marked absorption and enhancement effects. Nevertheless many increasingly successful efforts along these lines have been made and are dealt with in the next section. The use of empirical coefficients was suggested for electron-probe work by Castaing[3] and followed up by many others, notably Ziebold and Ogilvie,[182] but has tended to be less popular than the fundamental parameter methods. For X-ray fluorescence, however, the opposite is true and the empirical coefficient method is widely used and is slowly being perfected.

2. *Fundamental Parameters*

Early work towards providing a theoretically based relationship between fluorescent X-ray intensities and element concentrations was carried out by Sherman[183] in 1953 with later follow-up.[184-187] One of the weaknesses, however, lay in inadequate knowledge of the true primary radiation spectrum, with special reference to the ratio of characteristic to 'white' radiation. Gilfrich and Birks[188] set out to remedy this and made careful and detailed spectral measurements for several X-ray tubes. Later, Brown and Gilfrich[189] added to the information available by offering a means for calculating Kα and Lα line intensities from X-ray tubes and Castellano et al.[191] proposed a method for finding the percentage contribution of the characteristic radiation to the whole spectrum. Their finding for chromium was in agreement with the measurement of Gilfrich and Birks.[188]

This elucidation of the primary spectrum enabled Criss and Birks[190] to put forward the following formulae for relating intensity to concentration by the use of fundamental parameters with standards which need only be the individual pure elements. The symbols used are those already defined, where possible, and the remainder are consistent with them.

$$R_A = \frac{I_A}{I_{(A)}} = C_A \frac{\sum_{p=1}^{P_A} \frac{I_p \mu_{Ap}}{\mu_{Sp} \operatorname{cosec} \phi + \mu_{SA} \operatorname{cosec} \theta} [1 + F]}{\sum_{p=1}^{P_A} \frac{I_p \mu_{Ap}}{\mu_{(S)p} \operatorname{cosec} \phi + \mu_{(S)A} \operatorname{cosec} \theta}} \tag{16}$$

$$F = \frac{1}{2\mu_{Ap}} \sum_B D_B C_B \left(1 - \frac{1}{r_A}\right) \omega \mu_{AB} \mu_{Bp} \quad \times \left[\frac{\ln\left(1 + \frac{\mu_{Sp} \operatorname{cosec} \phi}{\mu_{SB}}\right)}{\mu_{Sp} \operatorname{cosec} \phi} + \frac{\ln\left(1 + \frac{\mu_{SA} \operatorname{cosec} \theta}{\mu_{SB}}\right)}{\mu_{SA} \operatorname{cosec} \theta} \right] \tag{17}$$

Subscript p: refers to primary radiation

I_p = the integrated intensity of the primary radiation over a small interval $\Delta\lambda$ (Gilfrich and Birks[188] chose $\Delta\lambda = 0.02$ Å)

P_A = the number of the primary wavelength interval $\Delta\lambda$, at which the wavelength λ is that of the absorption edge for element A

F = the correction for enhancement of the radiation of element A by radiation from other elements in the sample

$\sum_B$ = the summation for all elements B with characteristic radiation energetic enough to enhance the radiation of A

D_B = 1 for each primary radiation interval energetic enough to excite the radiation of B, and 0 for other values of p

ϕ = angle of incidence of the primary beam

θ = angle of emergence of the secondary beam

The considerable similarity between Equations 17 and 9 is to be expected because both account for enhancement of one element's radiation by another, after the primary excitation. The rather greater difference between Equations 16 and 1 is due to the major differences between X-ray and electron excitation. Iteration, again following the hyperbolic form of Criss and Birks[149] (Equation 15), is necessary because the concentrations are needed to calculate the intensities. Gould and Bates[192] have made extensive use of the formulae just discussed and found them to lead to successful results.

Stephenson,[196] however, states that the primary spectrum is still inadequately defined because the mass absorption coefficients at the higher energy end of the spectrum are imprecisely known. He attempts to eliminate this uncertainty by assuming an effective excitation energy just above the appropriate absorption edge and calculates an intensity for this assumed energy. Otherwise his absorption and fluorescence corrections have the same basis as Equations 16 and 17. He admits that this is at best an interim solution.

The approach of Ebel[194,195] is to make measurements with different angles of incidence and emergence of the radiation, and again thereby to eliminate necessity for absolute information about the spectrum.

Tertian[196] also deals with the problem of the primary spectrum and shows that the so-called 'effective' or, in his terminology, 'equivalent' wavelength is an inadequate concept and that it drifts with change in matrix.

3. Empirical Coefficients

The use of empirical coefficients to allow for interelement effects in X-ray fluorescence spectrometry dates back at least to Beattie and Brissey[197] in 1954 and a recent compilation by Rasberry and Heinrich[198] makes it clear that many subsequent workers, sometimes perhaps without realizing it, have followed the same path.

Lachance and Traill,[199] clearly acknowledging their debt to Beattie and Brissey,[197] Castaing[3] and others, pointed out that it was more convenient to 'rephrase' the equations and they proposed

$$R_A = \frac{I_A}{I_{(A)}} = \frac{C_A}{1 + \alpha_{AB} C_B + \alpha_{AC} C_C + \ldots + \alpha_{An} C_n} \qquad (18)$$

where

α_{ij} = a coefficient to allow for the effect of the presence of element j on the characteristic radiation from element i.

This simple form of correction, or something akin to it, has been found useful by many but has been acknowledged by most to be too simple. Claisse and Quintin[200] find that once again the primary spectrum is the cause of trouble and they propose second-order terms to cater for summation over a range of primary wavelengths. The difficulty about this approach is that it requires a larger number of standards because of the increased number of coefficients. Jenkins[201] has used the simple approach successfully but cautions that graphical procedures should be used to check that the system is staying on the rails. In another paper[202] he too warns against the danger of paying inadequate attention to the primary radiation.

Criss and Birks[190] compared the 'empirical coefficients' with the 'fundamental parameters' method slightly to the advantage of the latter. Subsequently Fatemi and Birks[203] pointed out that experimental errors in measuring the X-ray intensities inevitably led to inconsistencies between subsets of simultaneous equations similar in form to Equation 18. They show how such inconsistencies can be detected and give two methods for correcting the deficiencies. In the 'constant fractions' method the same fraction is added to each of the intensities and in the other method corrections are applied according to the 'least squares' procedure.

The most recent attempt to improve the empirical approach is by Rasberry and Heinrich[198] who suggest

$$\frac{C_A}{R_A} = 1 + (\alpha_{AB} C_B + \alpha_{AC} C_C + \ldots + \alpha_{An} C_n) + \frac{1}{1+C_A} (\beta_{AB} C_B + \ldots \beta_{An} C_n) \qquad (19)$$

Essentially their argument is that the α coefficients cater for absorption and the β's for enhancement. They demonstrate that enhancement causes a plot of intensity versus concentration to have a shape different from that of the simple hyperbolic curve for absorption, and that the last part of Equation 19 matches well with experimentally determined enhancement situations. Tertian[196] objects that absorption by a light matrix, such that the intensity of a heavy element is raised rather than lowered, is not fully catered for. It seems, however, that such a situation will be no less catered for than before and that enhancement should be more effectively dealt with. Probably the main objection to the method is that pure element standards still cannot be used, a total of (n-1) calibration points being required for each of the n elements present.

The Lucas-Tooth and Price[204] equation

$$C_A = P + I_A (Q + \Sigma \alpha_{ij} I_j) \qquad (20)$$

where P and Q are constants, is still used when computer capacity is limited[201] because only intensities occur on the right-hand side of the equation. Once again, however, the increasing availability of minicomputers is likely to decrease the need for such oversimplification.

C. Quantitative Energy-dispersive Spectrometry

Although the obvious first use for EDS was for rapid qualitative analysis, it was natural that tests of its potential as a quantitative tool should not be long delayed. In 1970 Myklebust and Heinrich[205] reported results on standard alloys obtained by EDS on an electron-probe microanalyser. They used the computer program COR referred to earlier,[150] and achieved remarkably good results using a detector with 500-eV resolution. They compared calculations done with peak and with integrated intensities, and the latter have consistently been used since. A year later Russ,[206] having the advantage of detectors with greatly improved resolution, had realized that, especially with electron excitation, the main difference between EDS and WDS lay in allowing for the higher background associated with the former, and had set about finding the most efficient method for determining and removing that background. He pointed out that an abrupt drop in background takes place at an energy above the peak but too close to it to be separated. This drop is due to the absorption edge for the element in question. At this time he defined a peak as a region of appropriate width rising at least twice the standard deviation above its surroundings. Using the associated minicomputer, such regions were detected and subtracted, each one a part at a time until no significant peaks remained. What did remain was called background and subtracted from the original. The same author[207] has now proposed and tried a solution based on frequency. He arranges electronically for the removal of the very-low-frequency nonlinearly varying 'overall' background and the high-frequency statistical variations. What is retained is the very high-frequency absorption-edge steps and the intermediate-frequency characteristic X-ray peaks. The effect is not only to remove background but to smooth peaks and very slightly improve resolution. Vannier and Sutfin[208] have also employed techniques already in use for gamma ray spectra to smooth EDS spectra.

The work of Reed and Ware,[209] however, covers in precise detail all the additional potential pitfalls to be avoided when dealing with EDS, as opposed to WDS, electron-excited X-ray spectra. The choice of energy range for optimum integration is set at approximately the FWHM[210] within which 68% of the total counts lie. They point out that if pulse pile-up rejection is not used, corrections for spurious 'sum' peaks (two quanta appearing as one of twice the energy) must be made, and that this is difficult. Escape peaks must also be corrected for. They have a height between 0.1 and 1.5% of the parent peak.[211,213] Ware and Reed[212] deal with the background problem but less empirically than Russ. They suggest the following equations.

$$I(E) = k[F(E, \chi, x_i) + F(E)]\, dE \qquad (21)$$

with

$$F(E, \chi, x_i) = [(E_0 - E)/E]\, f(\chi) \exp[-\Sigma(\mu_i \rho_i x_i)]. \qquad (22)$$

where

I(E) = the intensity of the background at energy E
k = a constant
F(E) = an empirical factor to be discussed
x_i = the thickness of an absorbing element i between the sample and the useful region of the detector
ρ_i = the density of material i

In Equation 22 the exponential term deals with absorption of the radiation at energy E, by the beryllium window, the gold electrode, and the silicon dead layer, at the face of the semiconductor detector. The f (χ) is that of Equation 5, the Philibert formula for absorption by the sample itself of the emerging radiation. The first portion of Equation 22 is Kramer's[214] expression for the intensity of the continuous radiation. The term F(E) in Equation 21 is an empirical term found to be constant down to about 3 keV. Ware and Reed[212] give figures for F(E) below 3 keV but stress that they are instrument-dependent.

Because of limited resolution, line overlap is also a more common problem in EDS. Reed[209] suggests that empirical correction using spectra generated by suitable standards is better than assumption of ideal gaussian peaks, because of incomplete charge collection in the detector and hence variable enhancement of intensity on the low energy side of the peak. He also discusses energy calibration, but this should change so little with modern equipment that it will soon cease to be a problem. Loss of resolution and possible peak shift, both due to the use of too high counting rates, will continue to provide difficulties, however, and can be dealt with reasonably only by not allowing the counting rate to become too high.

Solosky and Beaman[215] point out that the energy-dispersive spectrometer itself offers a means of determining, more accurately than can normally be done, the accelerating potential E_0 of the electron beam at the sample. In extreme cases, for example, an error of 1 keV in E_0 can lead to a 10% error in concentration. An accuracy of better than 80 eV is believed in Solosky and Beaman[215] to be achievable by studying the EDS spectrum on a cathode ray tube.

The same authors[216] made a survey of published quantitative results using EDS and compared them to their own experimental work and to collations of WDS-based work, all with electron excitation. Not surprisingly at this relatively early stage in EDS development, they found its errors to be much larger than those for WDS. Their conclusion was that the relative error of EDS was typically ± 6% at concentrations above about 20% and ± 10% for concentrations between 5 and 20%. This compares with less than ± 2% for the WDS work reported.

Desborough and Heidel[134] claim to have achieved relative errors of 1 to 5% for only 10 to

20 sec counting time. They use low operating voltages (10 and 15 kV) to allow increased beam currents without pulse pile-up, to reduce absorption corrections, and to use the energy region in which the detector is most effective (1.2 to 7.5 keV). Single-channel analyzers are used to permit higher count rates than can be allowed with multichannel analyzers. This last feature is unlikely to be popular because of the limitations it sets to qualitative analysis.

Most of the quantitative work with EDS has been on electron-probe microanalyzers, but some authors have used radioisotope sources. The work of Marr and Campbell[217] (and to a lesser extent that of Miller[218] with electron probe) is useful in showing, not so much the quantitative aspects, as the difficulties and possibilities when a local minicomputer is not available. Marr and Campbell used a time-sharing computer system and found it relatively cheap but tedious. The reading in of data via an ASR33 teletype took 5 min even though the multichannel analyzer had only 400 channels. Programs for peak location and intensity determination were written and used. The correction program thereafter was of their own design, but they discuss the possibility of using empirical coefficients and established multiple regression programs already written for timesharing systems.

The 'fundamental parameter' approach was used by Laine and Tukia[219] on Cu-Sb alloys, their source being an ^{241}Am ring. Their work is unusual in that their check is not against 'chemical' analysis but against compositions determined by X-ray diffraction using the same detector and electronics as for the X-ray fluorescence.

The work of de Jesus[220] on the other hand is based on empirical coefficients, initially of the Lucas-Tooth and Price[204] type, but then modified in an attempt to cater for the high scattered background. They are then applied, reasonably successfully, to iron, copper and zinc in ore fractions.

A third approach, which is not new[221] but is particularly convenient with EDS, is the use of thin samples. Rhodes et al.[59] demonstrated that the ratio of fluorescent to scattered radiation is higher for thin samples and since there are limitations on count rate with EDS the total fluorescent plus scattered radiation is limited. The gain in signal that can be achieved is the gain in fluorescent to scattered ratio, which in turn is roughly proportional to the ratio of secondary to primary absorption coefficients. They also showed that enhancement effects are negligible and absorption effects much reduced. Figures for detection limits (1σ above background) with Whatman 41 filter paper as a base varied from 26 ng/cm^2 for bromine to 150 ng/cm^2 for chlorine.

A similar approach was taken much further by Giauque and co-workers.[222,223] Their method involves thin uniform samples at less than the critical thickness for the radiation involved, a single thin film standard, and monoenergetic exciting radiation. For the last they used the molybdenum target transmission tube mentioned earlier[44] and as a standard they had an evaporated film of copper of 'thickness' 101 μg/cm^2. The formulae involved in the calculation of weight fraction of a particular element are as follows:

$$C_A = \frac{I_A}{I_{(S)}} \times \frac{L_{(S)}}{L_S} \times \frac{\ln M}{1 - M} \times \frac{m_{(S)}}{m_S} \times \frac{1}{K_A} \tag{23}$$

$$M = \frac{I_{A+D} - I_A}{I_D} = \exp\left[-(\mu_{SP} \operatorname{cosec} \phi + \mu_{SA} \operatorname{cosec} \theta) m_S\right] \tag{24}$$

$$K_A = \tau . \frac{r_A - 1}{r_A} \cdot \omega . f . T . \epsilon \tag{25}$$

where subscript D represents a target placed temporarily behind the sample to help determine M, and subscript P represents the monochromatic primary radiation.

L = the X-ray tube current used
m = mass per unit area, (g/cm^2)
τ = the appropriate photoelectric cross section for element A
f = the ratio of the intensity of the chosen line to the total intensity due to the energy level in question
T = the fraction of the radiation not absorbed between specimen and detector
ϵ = the efficiency of the detector for the radiation being measured.

Values for τ, r_A, ω, and f are all reported in the literature.[224-228] The value of ϵ is 1 except at higher energies (e.g., 0.79 for SrKα at 14.14 keV) and T is readily calculated using mass absorption coefficient data. K_A can, therefore, be calculated and relative values found in terms of the standard chosen (in this case copper). A table of calculated and determined values agree fairly well. The determination of M can be made from theoretical values or by measuring intensities with and without a target behind the sample. The ratio of the difference between the intensities with and without the target in position to the intensity with only the target there (Equation 24) gives the value for M, the absorption correction. The ratio of X-ray tube currents during measurement of standard and sample respectively is necessary because count-rate limitations do not always allow the same current to be used.

The theory is put to the test for a series of biological, rock, pottery, and air particulate samples. In most cases standard values or results from other techniques (e.g., neutron activation) are available for comparison and show acceptable agreement. The claims are directed particularly towards trace analysis, and concentrations of 1 ppm or less are achievable with signals three times the square root of the background. For air particulate samples the equivalent is 10 ng/cm^2 or less.

VI. SAMPLE PREPARATION

A. Powders

The general problem of heterogeneity was dealt with in Section V B 1 and the theoretical models proposed by Berry[172] and others[173] were mentioned. There are few solutions to the particle-size problem other than to reduce the size to a minimum as indicated, for instance, in the work of Ambrose[229] on iron ore sinter samples. He studied such factors as grinding time, mill load, initial particle size, and pelletizing pressure, and reached the common-sense view that grinding time had an important effect.

Claisse[230,231] has long had an interest in particle-size problems. One of the proposals[230] is to use an internal standard with absorption coefficient to match that of the element being measured. This is, of course, common practice for solutions. In another paper he and his coworkers[231] examine carefully the choice of diluents with the aim of avoiding heterogeneity effects.

For preparing discs from powdered geological samples Fabbi[232] has made a special die which allows the specimen to be cast and then surrounded and backed by a durable plastic.

B. Liquids

At first sight liquid solution methods appear to have attractive features for X-ray spectrometry.[233] Heterogeneity disappears, standards are easy to prepare, and the classical internal standard method of von Hevesy[2] is easy to apply. A closer look, however, shows up the weaknesses.[233] Concentrations must be closely controlled, scattering is high, intensities are reduced, bubble formation causes problems, irradiation may induce chemical reaction, and lighter elements become more difficult to arrange for. The last is overcome in one of two ways. Helium can be made to replace the air between sample and detector[234] and so reduce absorption of the longer wavelengths, or special sample holders can be designed to allow removal of the air. One such is by Hughes and Davey[235] who allow the vapor pressure over the liquid to be exerted on a window between the X-ray tube and the liquid. The secondary radiation, therefore, has only to traverse a short path in vapor and the rest is in vacuum.

Samples that already exist as solutions sometimes offer difficulties in the determination of the blank value. Spiking methods,[236] the addition of known quantities of the element being determined, are often helpful even for high concentrations and multielement solutions.[237]

C. Fusion

The use of fusion as a sample-preparation technique for X-ray fluorescence spectrometry did not become popular until relatively recently. Early samples tended to adhere to the crucible and were not always homogeneous, and strains caused cracking of a high percentage of beads. There was distrust concerning the potential loss of volatile material, and dilution caused lowering of intensity and loss of sensitivity. However, the increased intensities available from modern spectrometers have reduced the effect of the last point and have encouraged work towards removing the other objections.

Most of the earlier preparations were with borax and although some more recent authors still use it[238-241] there has been a movement toward preferring lithium borate.[242-249] Jenkins[174] points out that the reason commonly given for the change is the lower X-ray absorption of lithium but that it is in fact more reactive towards basic oxides than sodium borate and will often, therefore, produce a more homogeneous melt.

Crucibles made of platinum with 5% of gold, although expensive, are coming to be widely used[238,239,248,249] because of their 'nonstick' properties. Because it is easy to machine and cheap to replace, graphite is also popular as a crucible material.[242-248,250] The carbon produces no overt matrix effects but it is usually found that the glass discs must be ground and/or polished.[242,244] An unusual extra function for the graphite crucible is suggested by Wittman.[251] He grinds it up with the bead after casting and uses it as a binder to press a pellet, which is used for emission spectrometry as well as for X-ray fluorescence. Fabbi[246] also finds that grinding and pelletizing after fusion leads to higher accuracy for silicate-rock analysis.

The addition of a heavy absorber, usually lanthanum oxide[249,250,252] can reduce to negligible proportions matrix effects that would otherwise arise due to changes in concentration of other elements. The absorption due to the lanthanum oxide predominates over absorption by the sample elements.

The homogeneity that can be achieved by fusion was demonstrated by Smellie.[253] He prepared samples for electron-probe microanalysis by fusion in a molybdenum boat in vacuum and found them to be homogeneous on a submicron scale. But a cautionary note was sounded by Le Maitre et al.[247] They found that surface diffusion in lithium-borate-based discs, after prolonged (several hr) irradiation, produced increased count rates for aluminum, silicon, and phosphorus, but decreased count rates for sodium and magnesium. Removal of about 10 μm from the surface restored the original count rates.

VII. TRACE ANALYSIS

Because, whatever the technique, the skills of the analyst are employed to their limits by trace analysis the subject tends to be somewhat controversial and confusing. Part of the natural confusion is due to frequent failure to distinguish between the detection of very small masses and the determination of very low concentrations. Sometimes, too, the concentration limits quoted make startling reading because the method and degree of preconcentration are inadequately stated. Nevertheless, whether the interest is in ppm or in ng there is sure to be a particular facet of X-ray spectrometry whereby it can offer limits comparable to most other techniques.

The definition of the limit of detection varies widely from author to author[181] but the one quoted by Jenkins and de Vries[254] is a very reasonable one. It is

$$\text{Lower limit of detection} = \frac{3}{m}\sqrt{\frac{R_b}{T_b}}$$

where the subscript b refers to the background, R is the counting rate, T the counting time and m is the slope of the calibration curve of intensity against concentration. This is more comprehensive than the commonly used figure of twice the standard deviation of the background count rate $(\sigma_{R_b} = \sqrt{R_b/T_b})$. The factor 3 is roughly equal to $2\sqrt{2}$ which takes account of the fact that two measurements must be made, a peak and a background, thereby increasing the error by $\sqrt{2}$. The insertion of m is necessary to translate from intensity to concentration.

For a plane-crystal X-ray fluorescence spectrometer the limit of detection varies from about 100 ppm at worst to 1 ppm at best[254] for a counting time of 100 sec and an average matrix. At long wavelengths the sensitivity falls off because of inefficient excitation and absorption in the detector window. At short wavelengths, high backgrounds, poor resolution, and crystals too short to intercept the whole beam, account for a drop in sensitivity, but a less marked one than at long wavelengths. Klockenkaemper[255,256] also deals with the effect of instrument parameters on detection limits and finds that an improvement by a factor of three can be obtained by using a double crystal spectrometer.

Although techniques such as neutron activation and atomic absorption, optical emission, and spark source mass spectrometry can all achieve much lower limits than the average 10 ppm just suggested, all have their own disadvantages. The first is slow and is rarely fully under the analyst's control, the second is tedious for multi-element analysis, and the remaining two tend to be imprecise. It is, therefore, well worth considering whether or not preconcentration techniques can be made sufficiently simple and effective to allow X-ray spectrometry to compete.

Two basic methods have been successfully used for preconcentration: ion exchange and precipitation. The ion-exchange-paper technique is most fully documented in papers by Campbell, Spano, and Green[257] and by Campbell, Green, and Law.[258] They used both cation- and anion-exchange papers 3.5 cm in diameter and 0.03 cm thick, capable of collecting about 0.2 meq/disc.

The cation discs were found to be most efficient at a pH of about 2, whereas pH-values below 5.5 were recommended for the anion papers. Solutions were passed through the papers seven times to ensure efficient collection and for most ions, especially the cation, this resulted in more than 99% being retained. The sensitivity (counts sec^{-1} μg^{-1}) remained constant for transition elements up to 200 or 300 μg/disc. Detection limits (quoted as $3\sqrt{R_b}$ for a 10-min counting time) were as high as 5 μg for aluminum but as low as 0.05 μg for cerium, with many elements around the 0.1-μg limit. Concentration limits are naturally not quoted but one example is given in which Ca, Cd, Co, Cu, Fe, Mn, Ni, and Zn were determined at levels from 1 to 90 μg in 2-g samples of kidney tissue.

One of the few cations reported as being inefficiently collected was cesium, but Hooton and Parsons[259] found that mixed cation and anion exchange resins in one paper resulted in >97% retention of cesium. The same authors,[260] noting that the direction of filtration through the disc made no difference to the exchange process, designed a double flask unit with the paper clamped between. When filtration is complete in one direction the unit merely has to be inverted and the liquid then passes in the opposite direction. For determinations of the lighter elements by this or any other ion-exchange-paper technique, X-ray intensity measurements should be made on both sides of the paper to ensure that absorption effects within the depth of the paper are accounted for.

Some workers[261-264] have found it preferable to use resin particles rather than paper. The particles are merely agitated in the solution or the solution is passed through a bed of particles. Pressed pellets can be made from the resin beads as for normal powders. Internal standards can, of course, readily be added[262] and selective adsorption can sometimes be arranged by careful choice of resin.[263] Govindaraju[264] makes the point that fusion for rock samples removes the mineralogical and particle-size problems but leaves absorption and enhancement effects. He puts the fused powdered sample into aqueous suspension with strongly acidic cation-exchange resin for 3 hr with agitation. He then puts a single layer of resin beads onto adhesive paper and uses this as his sample. The high dilution (1:70) and the 'thin film' nature of the sample lead to linear plots of intensity versus concentration for elements from magnesium to iron.

In some early work, Luke[265] used very small ion-exchange discs with a curved-crystal milliprobe. Later, however, he developed extensive coprecipitation methods[266] for 69 elements in the X-ray spectrometric range out of a possible 72. Among the less selective reagents that he found to be suitable for precipitation were sodium diethyldithiocarbamate, cupferron, ammonia, and hydrogen sulfide. To ensure quantitative precipitation of trace elements he found it necessary to add up to 200 μg of a suitable coprecipitating element. Membrane filters with pore sizes from 0.8 to 5 μm were used. Sensitivities achieved were from 2 counts sec^{-1} μg^{-1} for magnesium up to 300 counts sec^{-1} μg^{-1} nickel, titanium, and scandium. For these three elements as little as 20 ng could be determined. More recently, with Mitchell and Northover,[267] Luke was able to achieve 8,000 counts sec^{-1} μg^{-1} for nickel with slightly lower values for neighboring elements. Two factors led to the improvement. A reduction of the area of collection was pioneered by Kessler and Vincent.[268] The precipitate is now directed and concentrated into a 'microdot,' 0.1 in. in diameter. This permitted reverting to the curved-crystal milliprobe for more efficient X-ray collection from such a small sample. By such means particulate impurities from ultrapure reagents were monitored down to 1 ppb. The elements lithium, berylium, and phosphorus were also determined indirectly by precipitation methods.[269]

Independently of Luke's work, Pueschel[270-272] was pioneering the use of 1-(2-pyridylazo)-2-naphthol as a complexing agent, chiefly for manganese, iron, cobalt, nickel, copper, and zinc. He was able to detect as little as 0.1 μg in 50 cm^3 of solution. The use of the Weisz[273] ring oven technique is mentioned by Pueschel and enlarged upon by Ackermann and co-workers[274] for use with filter paper.

The use of X-ray fluorescence to detect[275] and even determine[276] the specific elements in thin-layer chromatograms has been described. Houpt[276] constructed a cylindrical drum round which the chromatogram was wrapped and which could be revolved over a slit in a normal X-ray spectrometer sample holder. He achieved a spatial resolution of about 2 mm with detection limits of 10 μg for chlorine and 2.5 μg for bromine.

Both the ion-exchange and the coprecipitation techniques (sometimes used together[277]) are suitable for liquid-effluent monitoring. Monitoring of particulate air pollution collected on cellulose filters, or more commonly nowadays on membrane filters, is just as obvious a candidate for X-ray spectrometric measurement. Gilfrich, Burkhalter, and Birks[278] concur, quote some work already done, and set out to determine which X-ray spectrometric technique is most suitable (excluding electron excitation). Their very comprehensive study splits the detection possibilities into sequential wavelength dispersion, simultaneous wavelength dispersion, and energy dispersion. For excitation in the first case they investigated the use of X-ray tubes with Cr, Rh, and W targets.

With EDS they used the radioisotope sources ^{55}Fe and ^{109}Cd; W and Mo target tubes directly; and the former tube indirectly with Mn, Cu, Ag, or Cr-Zr as fluorescers. The work on multichannel WDS instruments was carried out with the manufacturer's cooperation and is not detailed. Having made measurements with the equipment at hand, they extrapolated their results to match what they believed to be acceptable present-day upper limits for the excitation sources or for the detector count rate. Their table of detection limits, for various X-ray techniques is given in Table 3.

It can be seen that with direct X-ray-tube excitation the limits, for the elements given, are similar for EDS and WDS. This is, however, somewhat misleading. Wavelength dispersion can almost always win with actual samples because its superior resolution allows a small quantity of a given element to be detected in the presence of a much larger quantity of an element adjacent in atomic number. Also the predominance of one or two elements reduces the available count rate and increases the background for the minor constituents with EDS. The much lower detection limits given for particle excitation are somewhat artificial in that filter paper could not survive the beam currents used, and special standards with carbon and other thin (10 to 20 μg cm^{-2}) backing materials had to be made. Gilfrich et al.[278] come down in favor of multichannel WDS instruments for particulate air pollution monitoring and quote 1 to 10 ng cm^{-2} as limits for many elements with a counting time of 100 sec. They are careful to point out, however, that with such an instrument there are limitations on changing the elements monitored and that a qualitative survey facility with an energy-dispersive detector makes a convenient addition. If only one or two elements have to be measured, then EDS is simpler and cheaper.[279] Rhodes[59] and Wood[280] both give practical examples of the detection of tens of nanograms per square centimeter on filter paper with energy-dispersive detectors.

Most of the work with high-energy-particle excitation has already been mentioned (Section III E, References 64 to 76). Without exception the aim has been towards trace analysis, and in weight terms has undoubtedly been successful when compared to X-ray excitation. Both Johansson[66,281] and Duggan[67] demonstrate that a few picograms can be detected. Johansson[66] for example shows a clear peak for 30 pg of chromium. This compares with the nanogram amounts determined by Mitchell et al.[267] with X-ray excitation. Most of the samples, however, for particle (other than electron) excitation are presented as thin films on a thin backing. If this is not done much of the advantage of low backgrounds[73] and no absorption corrections, begins to disappear. A more reasonable comparison would, therefore, seem to be possible in terms of weight per unit area and then the difference disappears. Umbarger et al.[68] show graphs for 1- and 2.25-MeV protons and for 30-MeV alphas covering a range of roughly 2 to 200 ng cm^{-2}. Now this is the same range, approximately, covered by Table 3 and in the accompanying remarks about Gilfrich's[278] work. Shabason and colleagues[76] remove one of the restrictions and use thick samples. To retain the other advantages, they use 40-MeV oxygen ions with a range of only 200 μm in carbon. But the concentration limit is no better than about 10 ppm, and that is in a light matrix such as Li_2CO_3. While the technique is still undoubtedly a promising one for trace analysis, it would seem that early optimism must now be tempered with some caution.

Electron excitation has so far been excluded from this study because with thick samples the background is high and the concentration detection limits are poor. Electron-probe techniques have, however, no rival when the volume of sample analyzed is considered, and hence are very competitive in weight terms. The conventional electron probe microanalyzer will excite X-rays from a volume of about 1 μm^3 and will allow 0.1% of elements in this volume to be determined. This

TABLE 3

100-sec Detection Limits for Various X-ray Techniques, ng/cm^2

	Al	S	K	Ca	V	Fe	Cu	Zn	Se	Br	Zr	Au	Pb
WAVELENGTH DISPERSION													
X-ray tube excitation													
as measured (900 watts)													
Cr tube	360	52	3	10	53	150	160	180	820	390			1,000
Rh tube	85	13	18	29	33	30	49	51	150	210			260
W tube		52			29	36	40		100	160			
Extrapolated													
to 2,500 watts													
Cr tube	220	31	2	6	32	90	96	110	490	230			600
Rh tube	50	8	11	17	20	18	29	31	90	130			160
W tube		31			17	22	24		60	100			
ENERGY DISPERSION													
Isotope excitation													
as measured													
7 MCi ^{55}Fe*				110	180								
70 mCi ^{109}Cd				6,200	2,100	2,200		1,400	420		230		700
Extrapolated													
to 150 mCi													
^{55}Fe				84	130								
^{109}Cd				3,200	1,100	1,200		740	220		120		370
Fluorescer excitation													
as measured (900 watts)													
Mn				58	51								
Cu				62	68	44							
Ag				310	360			180	69		50		190
Cr–Zr				84		350		210	44				
Extrapolated													
to 2,500 watts													
Mn				27	24								
Cu				28	31	20							
Ag				150	170			84	31		23		84
Cr–Zr				38		160		100	20				

*Measurement with ^{55}Fe made for 2,000 sec because of low activity.

**0.002 sr aperture between X-ray tube and sample.

†150 Watts tube power with aperture produced count-rates of: Mo, 5,000 counts/sec; W, 10,000 counts/sec; W with filter, 3,500 counts/sec. At these count-rates, detector resolution varied from 400–500 eV.

††Ion measurement made for time necessary to accumulate 5 μC at beam dump. Approximately 100–200 sec.

TABLE 3 (continued)

100-sec Detection Limits for Various X-ray Techniques, ng/cm^2

	Al	S	K	Ca	V	Fe	Cu	Zn	Se	Br	Zr	Au	Pb	
X-ray tube excitation as measured (150 watts)**														
Mo tube						350	160	120		100	48			110
W tube						33	34	39		160	110			190
W tube–Ni foil				570	220	140	90	120		110	81			110
Extrapolated to 10,000, c/s†														
Mo tube						160	71	53		44	21			49
W tube						19	20	22		92	63			110
W tube–Ni foil				220	84	53	34	46		42	31			42
5-MeV ion excitation as measured (5 μC)††														
Protons					1				2			1	5	
Alpha particles					1							10	20	
Extrapolated to 50 μC														
Protons					0.2				0.5			0.2	1	
Alpha particles					0.2							2	5	

From Gilfrich, J. V., Burkhalter, P. G., and Birks, L. S., *Anal. Chem.*, 45, 2002 (1973). With permission.

means 10^{-14} g, at least two orders less than for the heavy-particle excitation just discussed.

To improve upon this it is necessary to use thin samples, because the initial resolution limitation lies, not in the diameter of the electron beam but in internal electron scattering. For biological studies, thin sections are suitable samples anyway and Russ[115] considers what can be achieved in an electron microscope with Epon and freeze-dried sections. He found that for thicknesses up to 2,500Å the excited volume could be represented by a cone with top diameter equal to that of the electron beam and a half angle of 24 to 29° for Epon, but only 3 to 5° for freeze-dried sections. This meant mean diameters for X-ray production of about 1,000Å for the plastic and 300Å for the freeze-dried section with a 200-Å beam. With a practical sample containing particles of CaB_6 he obtained a linear plot of intensity against concentration which when extrapolated to two sigma above the background gave a quoted mass of 2.7×10^{-18} g. The silicon detector was brought to within 5 mm of the sample to ensure efficient collection of the X-rays.

Even more startling is the work of Ecker.[114] He evaporated Al, Ti, Ag, and Au in varying thickness onto 200Å films of carbon. His plot is linear up to a few hundred Ångströms and the lowest actual plotted point is at 3×10^{-3} Å. The claim, therefore, that down to 10^{-3} monolayer can be detected seems well justified. For aluminum this represents about 0.05 ng cm^{-2}, a factor of 20 below the nearest comparable figure so far mentioned. The detection at this level was by WDS with a transmission electron microscope and a current of 2 μA. Because of the high current, the resolution was relatively poor at about 2 μm. Nevertheless this means that the emitting volume weighed only 1.5×10^{-18} g (for aluminum). With a scanning electron microscope and EDS the limit of detection was no better than 0.1 monolayer, because of interference from other peaks due to contaminants in the system.

The reasons why, in spite of theoretical predictions, electrons seem capable of producing higher sensitivity in terms of mass per unit area than any of the other excitors lie in the technicalities rather than in failure of the theory. Ecker's samples were supported on 200-Å carbon films which in turn required the support of electron-microscope grids. The grids provided no interference because the electron-beam diameter was small compared with the spacing between grid bars. Johansson's[281] sample-support films for proton excitation had thicknesses of 40 μg cm^{-2} (~ 1,700 Å). Ecker was, therefore, able to take advantage of the fact that X-ray cross sections for electrons are comparable to those for heavy particles (Figure 5). At the same time he was able to keep the bremsstrahlung to a minimum by means of his very thin substrate. Even then he says that half the background is due to scattered electrons striking other parts of the equipment. The other factor is the now frequently mentioned difference in resolution, and hence in signal-to-noise ratio, between WDS and EDS. Johansson's and all comparable work was with a silicon detector and with a similar detector Ecker's sensitivity was two orders of magnitude poorer than for wavelength dispersion.

Altogether it would seem that the field of trace analysis is still wide open for advance. At present for practical work, such as air-pollution studies, true X-ray fluorescence probably with multiple WDS[278] has the edge; for biological and thin-film studies electron excitation[114,115] seems to be winning; whereas heavy-particle excitation[64-76] has still to prove its real value.

VIII. LIGHT-ELEMENT ANALYSIS

Although it is now nearly 20 years since X-ray spectrometry was first used for practical analysis in the Be to F range,[282] effective progress has been slow and uncertain. The chief reason lies with the very high absorption coefficients so that any window, however thin, between sample and detector is undesirable. In the X-ray fluorescence field this is compounded by the very low fluorescence yields[283] for the light elements. Since the early work of Henke[45] there has been little progress with X-ray excitation. The work of Schoenfeldt and Pluchery[54] mentioned earlier (Section III B), is one of the few recent attempts in this area.

Electron excitation with X-ray cross sections that increase with decrease in atomic number,[64] has been slightly more successful. Franks[284] has worked steadily towards the improvement of ruled diffraction gratings for X-ray work and has designed, in conjunction with Stedman and Braybrook,[285] a spectrometer based on the Rowland circle principle with both the source and the detector constrained to move around the circumference of the circle in terms of their polar coordinates with respect to the pole of the grating. With a diamond sample, a count rate of 7,800 sec^{-1} with a peak-to-background ratio of 310 was measured. Even higher signal-to-noise ratios were achieved but with a reduction of the signal. Somewhat similar results were obtained by Grasserbauer and Weinrotter[286] using a grating with a blaze angle of 1° 33′. They obtained 16,000 counts/sec from graphite but with twice the slit width and a signal-to-noise ratio of only 27.

The use of a grating for dispersion has the advantage of producing the whole spectrum simultaneously, but apart from the early work with photographic detection[282] little or no use has been made of this feature, and there has in fact been a preference for crystal or rather pseudocrystal dispersion. The method for putting down successive layers of crystalline materials, usually stearates, with interlayer spacings of around 100 Å was described by Blodgett and Langmuir,[110] and such crystals are in daily use on many electron-probe microanalyzers.[287] Grasserbauer[286] makes a comparison, unfavorable to the crystal, between his grating and a lead stearate spectrum from Al_2O_3. The oxygen and a carbon contaminant peak are shown without interference in the grating case but with marked interference from higher-order AlKα lines in the crystal spectrum. These could have been removed or reduced by pulse-height discrimination together with the first-order AlKα diffraction from the mica support for the stearate. More serious is the interference between the wanted K lines from the light elements and L and M lines from heavier elements.[288] Scott[289] finds that careful choice of analyzing crystal helps with this problem, but that peak shift and change in band shape due to variation in the valence band structure are more difficult to cater for. Elimination of errors from quantitative work is more difficult for L spectra than for K, and as always, the need for accurate mass-absorption-coefficient data is acute.

The changes in peak shape have of course, been used by many to obtain information about the state of combination of the element being studied and, while electron spectroscopy of various kinds is tending to take over this role, useful work is still being done.[290-293] Solomon and Baun[290] used a time-sharing computer system to collate and smooth the spectra obtained from an electron probe with an automatic stepping motor control system. With the system functional they were able to use it to characterize materials,[291] and to distinguish, for example, among Cu, Cu_2O, and CuO. The work of Poole[293] is unusual in one or two respects. He uses electron excitation but with the instrument referred to earlier[11] offering a 1-cm^2 area of scan. The crystal is OHM (octadecyl hydrogen maleate) and the study is for carbon in sedimentary rocks over the range of 0.8 to 12% carbon. Some of the carbon is present as graphite and some as calcium carbonate. The peaks occur at 45.48° and 44.97° respectively and the ratio of intensities at these two positions allows the proportions of the two forms to be determined.

In the work dealt with so far in this section the detector was a thin windowed flow proportional counter. The use of a silicon detector for carbon,[30] nitrogen, and oxygen[39] was mentioned in Section II F. Again the relatively poor resolution will make the chances of interference greater but this time there may also be a slight advantage in that peak shifts will have less effect on the overall intensity, which can be high due to close approach to the sample. Long-term protection of the detector surface, however, remains a problem. The other detector whose potential has not yet been fully explored is the channel multiplier.[294] If used in the form of a channel plate (many channel multipliers of diameter, say, 20 μm, fused together) with suitable electrode arrangements, simultaneous detection of all the spectrum lines from a diffraction grating might be possible.

The Ross filter method (Figure 1) has been applied to light element determination.[295] Pichoir[296] has used gases as filters with the pressures adjusted to ensure matching absorption outside the range of interest.

Another simple suggestion to separate peaks in the 15- to 80Å range is that made by Herglotz[297] and others,[298] who use the dependence of critical angle of reflection on wavelength by oscillating a mirror through a small angle near grazing incidence and detect with an open-window photomultiplier. Holliday,[299,300] who has done much of the pioneering work in soft X-ray spectrometry, reviews the subject, especially as applied to metal surfaces.

IX. APPLICATIONS AND FUTURE DEVELOPMENT

A. General

Applications for a topic such as X-ray spectrometry can only be covered in somewhat broad and sweeping terms with, perhaps, pin point examples. But there is a close correlation between present applications and future developments of a technique. The user who sees the strengths and weaknesses of the method can continually exploit the former and eradicate or side-step the latter, and in so doing carry the subject into fresh territory both as regards technique and potential application.

The two main application areas are, of course, metallurgy and geology but the spread is now throughout industry covering cement, glass, paint, oil products, and plating. Environmental and forensic applications are perhaps the most rapidly developing ones, while biological possibilities have always existed and are steadily being expanded.

B. Metallurgy

Until relatively recently the optical spectrometer reigned supreme in the steel works. By degrees, however, the X-ray spectrometer has succeeded in achieving consort status. That success has not always come easily is evidenced by the large number of papers dealing with correction procedures for matrix effects in ferrous alloys.[301-306] Stainless steels always tend to be an early target for anyone trying out a new mathematical model.

Electron-probe microanalysis has added substantially to knowledge about heterogeneity,[307] oxides[308,309] and carbides[310,311] corrosion problems,[312] and a host of other facets of steel making and steel using.[313] This is an area in which the relatively cheap scanning electron microscope (SEM) allied to an EDS system can provide qualitative and semiquantitative information very rapidly and efficiently.

At the other end of the scale, the very large and complex X-ray fluorescence spectrometer, probably simultaneous and certainly WDS, should take over process-control analysis in many steel plants.[82] In many, if not most, other areas (glass making is an exception) the difficulty of adequate, rapid, automatic sample preparation rules out the possibility of a complete process-control loop. In steel making, however, automatic quenching and surface-grinding procedures can be made sufficiently reproducible to allow the loop to be closed.

Many other alloys – aluminum,[314,315] copper,[316] titanium,[317] zirconium,[318] and tin/lead[319,320] among them – have been analyzed successfully by X-ray fluorescence, although the last example is one of the more difficult ones because of the segregation of lead and tin[320] even after relatively short storage times at room temperature. In general, however, the sample preparation of metal alloys for analysis by X-ray spectrometry, with excitation by X-rays, electrons, or radioisotopes, is usually sufficiently simple to ensure an expanding future for the technique in this area.

C. Geology

A growing topic, sometimes on the borderline between metallurgy and geology, is on-stream analysis in mines and similar environments. Some of these units are large, simultaneous WDS instruments[321,322] monitoring a dozen or more elements and sometimes more than one stream. They are very expensive installations and yet the problems of heterogeneity may still limit their effectiveness. An alternative is the use of several radioisotope sources with no problems about situation and some potential advantages in relation to heterogeneity.[323] Watt and co-workers[324,325] have made considerable progress for mineral processing plants in Australia with radioisotope X-ray techniques. For tungsten ores Lubecki and Vogg[326] use nondispersive spectrometers and obtain good agreement with activation analysis. Papez and Cameron[327] discuss the wide application of nondispersive techniques to the basic metal industry, from mineral processing to the finished product. If an energy-dispersive detector is added, the versatility of radioisotope systems is increased and there appears to be a bright future for this combination.[98,328]

The growth of fusion as a sample-preparation technique stemmed mainly from the needs of geologists.[252,329] Until X-ray spectrometry arrived geological analysis tended to be slow and tedious. The multi-element possibilities of the X-ray techniques was seized upon and exploited to the fullest.[330,331]

The use of matching standards for electron-probe work in geology is even more fraught with difficulty than in metallurgy,[332] but a few natural samples can be found that are sufficiently homogeneous.[333] Nevertheless, geologists make almost as much use of the electron probe as metallurgists.[334,335]

D. Miscellaneous

As well as being used in steel and mineral-processing plants, the large simultaneous multielement spectrometers find application in cement works and glass factories and are beginning to be applied to environmental studies.[278] Wherever there is a need for precise quantitative analysis for more than one or two major constituents on large numbers of very similar samples, there will be a future for the simultaneous spectrometer. It will gradually become more powerful, more precise, more automatic and, occasionally, more versatile but the only major change is likely to be the addition of an energy-dispersive channel. Even that will not often be required.

Such a channel will be of more value in the sequential WDS instrument which will always provide the backbone of X-ray spectrometry. The normal sequential instrument is now in use in an enormous number of environments, from plating to plant research and from pharmacology to forensic science. It is rapid, versatile, and precise for quantitative analysis, but it is relatively slow for qualitative analysis. The addition of a rapid qualitative EDS channel should not pose too difficult a design problem. The very-light-element area is still the annoying gap. It seems likely that in spite of developments like the Sahores tube,[49] users of sequential instruments will settle for reasonable ability to determine fluorine and no lighter element.

The electron-probe field is a different matter. It would appear to have considerable development potential left. In the light-element field it is in any case better than X-ray fluorescence, but little X-ray spectrometric advance for light elements is likely because of the capabilities of electron spectrometry with the same primary beam. Nevertheless, some improvements in crystal and grating instruments seem likely. Otherwise the spread is both up and down; up, in the sense that more X-ray information is being extracted from very-high-resolution electron microscopes of various sorts; down in connection with cheaper scanning electron-beam instruments that provide information rather than that from an optical microscope, and simultaneously give semiquantitative X-ray spectrometric information.

The down-to-earth analyst will not often employ the 1-Å resolution transmission electron microscope but the 500-Å resolution SEM with EDS attached should soon be a tool within his means, rarely capable of providing the final quantitative determination but often pointing him in the right direction or revealing the true problems.

On a more sophisticated basis, manufacturers are already taking four initially separate building blocks: the electron probe, the wavelength-dispersive X-ray spectrometer, the scanning electron microscope, and the energy-dispersive spectrometer. These four are being designed together to combine the quantitative accuracy of the first pair with the qualitative versatility of the second.

The future of high-energy-particle (including electron[53]) excitation is still in the balance. If the initial promise for much improved trace analysis, especially for pollution applications, can be fulfilled, then proton excitation will probably gain ground. It has still to be proved, however, that the ppb analyses achieved with X-ray excitation[267] and the 10^{-18}g detection limit for electron excitation[114] can be matched, far less surpassed.

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