THE PRESENT STATUS OF ELECTRON PROBE MICROANALYSIS

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ABSTRACT

Few other analytical methods have expanded so rapidly as electron probe microanalysis during the past 10 years. The number of elements that can be determined or detected extends from beryllium to uranium and concentrations in the range 0·1–100 per cent can be dealt with. This has been made possible by the introduction of new analysing crystals and counting systems. The application of computer programming in conjunction with the various microprobe signals has allowed the development of valuable new methods for structural analysis. Even in commercial instruments, the electron beam can now be focused down to a diameter of 0·15 μm, hence the resolution of backscattered or secondary electron images is excellent and a large amount of information can be gained on the topography and morphology of solid substances. When integrators with proper discrimination are used, new information on diffusion systems, etc., in solid materials can be obtained. With all these possibilities, the position of electron microprobe analysis is now very strong. In addition to the use of x-rays for quantitative work, many other signals arising from the interaction of electrons with the target can be utilized.

INTRODUCTION

Electron probes have found a very wide spectrum of applications in science and technology, as well as for analytical purposes; however, presently available techniques by no means represent the final limits of development of this relatively new method. In the United Kingdom, many distinguished scientists are working on the development of electron probes. A survey of electron probe microanalysis from the standpoint of analytical chemistry rather than physics or physical chemistry may provide further impetus to still broader analytical applications of this elegant technique.

A backward glance over the past 60 years shows the tremendous progress that has been made in the field of analytical chemistry with regard to the reduction of limits of detection. In 1910, the limits of detection were generally of the order of 10^{-2} per cent and sample weights were generally in the range of 1–10 g. Today, sample weights of 1–10 mg are used wherever the homogeneity of the sample allows; the gradual decrease in general sample weights is shown in *Figure 1*. This decrease has, of course, been made possible by the improving limits of detection of new analytical methods; typical detection limits for a variety of currently used techniques are shown in *Table 1*. It can be seen that
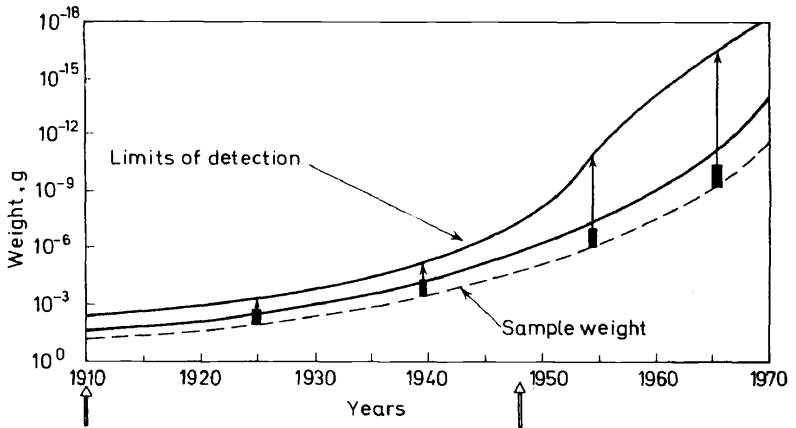
Figure 1. The historical development of sample weights in analytical chemistry

Table 1. Limits of detection of different techniques

Method	Limit of detection (g)
(Mass of an electron	9×10^{-28})
(Sex attraction of the bee	10^{-20})
Olfactory sense	10^{-18}
Electron microprobe	10^{-16}
Fluorescence microscopy	10^{-14}
Mass spectroscopy	10^{-13}
Emission spectroscopy	10^{-12}
Ring oven	10^{-12}
Absorption spectroscopy	10^{-10}
Spot tests	10^{-7}–10^{-10}
Electrochemical micromethods	10^{-9}
X-ray fluorescence	10^{-7}

the electron microprobe offers the greatest sensitivity of any instrumental technique.

In recent years, the use of electrons as analytical reagents has increased to a very great extent. In fact, it appears that the current development in this field is similar to the upsurge of interest in electrochemical methods some 50 years ago, when these procedures were added to the conventional gravimetric and volumetric methods which were then the major tools of analytical chemistry.

It may be useful briefly to define electron beam analysis and electron probe microanalysis. Electron beam analysis involves the use of the signals obtained from the interaction of an electron bombardment with the surface of a sample. Electron probe microanalysis is basically the same, but the electron beam is very finely focused and impinges on the particular point at the surface of the sample whose chemical composition is to be determined. Essentially, the electron beam is nothing more than a reagent—a relatively expensive reagent, but one which possesses many advantages. From the analytical point of view,

one might say that the acceleration voltage and the beam current represent the 'concentration of the reagent', and the focusing of the beam its 'purity'.

The price of an electron probe analyser is now not excessive; if it is considered that such equipment has a useful life of 10 years, the cost per hour of normal usage is in the region of $5–8.

Table 2. Comparison of the limits of detection for elements with atomic number 5–16

Element	Limits of detection (weight %)		
	Macroprobe	X-ray fluorescence	Microprobe
B C Al Si P S	} 10 × 10⁻³ } 1 × 10⁻³	— } 10 × 10⁻³ 100 × 10⁻³	} 3 × 10⁻³ } 1 × 10⁻³

In electron beam or electron probe analysis, the main concern is with primary x-rays. Both methods have the great advantage compared with x-ray fluorescence analysis, where secondary x-rays are measured, that the limits of detection for light elements are much better[1] (Table 2). The main difference between microprobe and macroprobe analysis lies in the diameter of the electron beam and thus in the current load of the sample. The ratio of the beam area to sample area is $1:10^8$ for the electron microprobe and $1:10$ for the electron macroprobe, hence the thermal load in the former method is much higher[1]. A comparison of the 'current load' for the two different techniques is shown in Table 3. Provided that the samples being analysed possess good electrical conductance properties, the difference in current load is of no importance, but non-conducting materials may be difficult to analyse because of changes in composition caused by the irradiation.

Table 3. Comparison of the 'current load' in microprobe and macroprobe analysis.

	Microprobe	Macroprobe
Specimen area	$3 \times 10^8 \ \mu m^2$	$3 \times 10^8 \ \mu m^2$
Beam diameter	$2 \ \mu m$	$4000 \ \mu m$
Area of the electron probe	$3 \ \mu m^2$	$1 \times 10^7 \ \mu m^2$
Specimen current	5×10^{-8} A	2×10^{-5} A
Specimen current/μm^2	5×10^{-8} A	2×10^{-12} A
Area of the electron probe/ specimen area	10^{-8}	3×10^{-2}

SIGNALS OBTAINED BY ELECTRON BOMBARDMENT

The interaction of a finely focused electron beam of high energy with a sample yields a variety of signals. The principal signals which are used in microprobe analysis are shown in Figure 2. In addition to these signals, there is
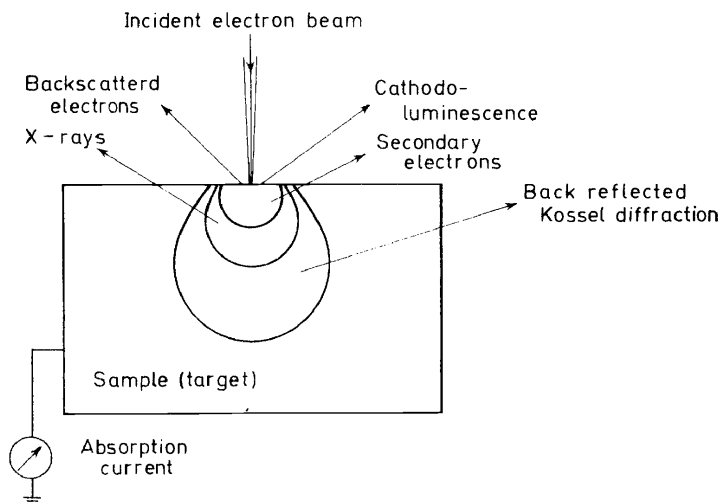
Figure 2. The principal signals utilized in electron probe microanalysis

Table 4. A summary of the information available from the different signals

Signal	Information
X-rays	Kind and concentration of an element
Absorbed electrons	Average atomic number
Backscattered electrons	(a) Average atomic number
	(b) Relief of the surface
Secondary electrons	(a) Relief via low energy electron collectors
	(b) Elemental analysis via Auger electrons
Transmitted electrons	Internal structure

the possibility of production of Auger electrons by x-rays already generated in the sample; and if the sample is thin enough, valuable modifications such as microradiography, transmission electron microscopy, etc., become available. *Table 4* summarizes the nature of the information that can be acquired from the different types of signals produced.

THE HISTORICAL DEVELOPMENT OF ELECTRON PROBE ANALYSIS

There is no doubt that it was Moseley[2] who first made a microprobe analyser by using a simple electron gun in a vacuum tube (*Figure 3*), and that he fully realized the great value of this discovery to analytical chemistry. But for Moseley's tragically early death, electron probe analysis might have arrived much earlier on the analytical scene. It is worthwhile to quote his statement made in 1913:

'The prevalence of lines due to impurities suggests that this (irradiation) may prove a powerful method of chemical analysis. Its advantages over ordinary spectroscopical methods lie in the simplicity of the spectra and the impossibility of one substance masking the radiation from another. It may lead to the discovery of missing elements and it will be possible to predict their characteristic lines.'

In Moseley's method, a trolley carrying various samples as targets was drawn under the electron beam and the characteristic x-rays resulting from the irradiation were measured photographically. About 25 years later, von Ardenne[3] used a finely focused electron beam for the excitation of primary x-rays and measured the backscattered electrons, and rather later, Möllenstedt worked on similar principles. According to Birks[4], Hillier in the United States was the first to receive a patent for the use of such an electron beam for chemical analysis in 1947, but he does not appear to have pursued the subject further. In any case, the first paper on this subject was presented in Delft in 1949 by Castaing and Guinier[5]. The original apparatus of Castaing, which he called 'microsonde électronique', was based on a French electron microscope,
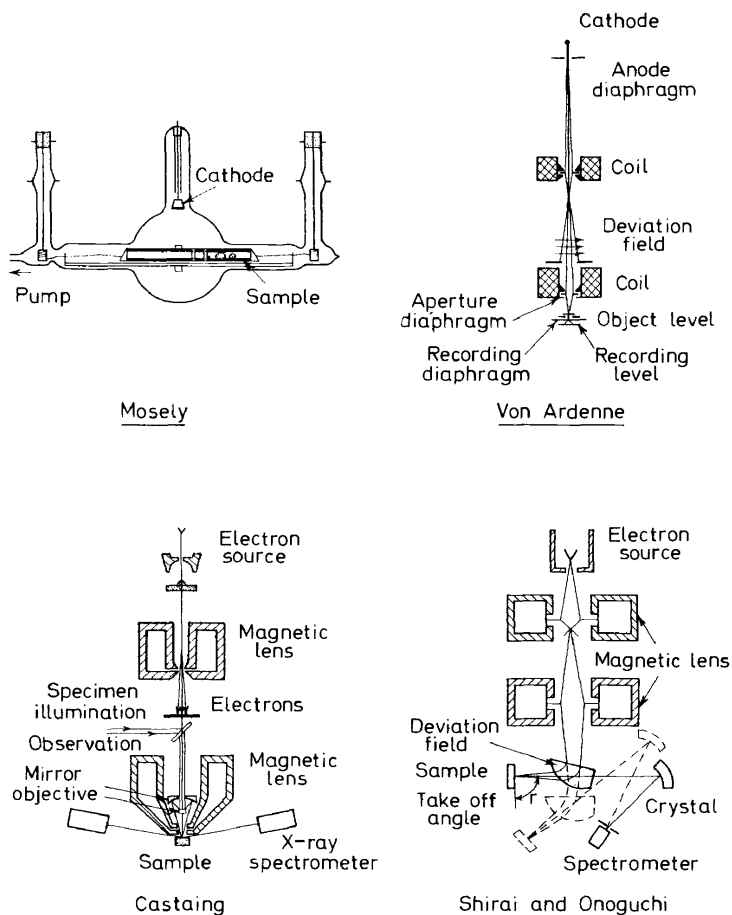

Figure 3. Development of instrumentation for electron probe analysis

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and some six years later, an improved instrument for electron probe microanalysis became commercially available. In their first paper[5], Castaing and Guinier not only outlined the principles of the construction of an electron probe microanalyser, but also laid the foundations for quantitative analysis. The instruments that are now commercially available have achieved a very high degree of sophistication.

Basically an electron microprobe analyser consists of: (i) an electron optical system for the formation of a fine electron beam of high intensity; (ii) a visual optical system for observation of the sample surface and cathodoluminescence; and, most important, (iii) a system for the performance of x-ray analysis, and, preferably, also for the detection of other signals.

There are so many possible different arrangements of the basic units that it is impossible to give more than a brief coverage. Considering only the take-off angle which varies[6] between 6° and 90°, it seems in the first instance that a 90° take-off angle would be best from the point of view of x-ray absorption, because the characteristic x-rays excited by the electron bombardment in the sample have then the shortest route for emergence and thus undergo minimal absorption in the sample. Shirai and Onoguchi[7] constructed an instrument which allows the use of such a high take-off angle; a high signal-output could be obtained and the signal was not highly dependent on the production of a very finely polished surface (*Figure 3*). The larger the take-off angle, the smaller the absorption corrections, but the larger is the fluorescence correction. The variety of take-off angles in the instruments available can be explained according to whether an excessive absorption correction or fluorescence correction is deemed the more important.

Analysing crystals

The development of analysing crystals is also of great importance. The difficulties encountered in the analysis of the light elements lie in the discrimination and measurement of radiation of long wavelength. Very high demands must be met with regard to the sensitivity of the dispersion and detector systems, so that the excitation potential can be kept small (8 kV or less) and so that the optimal resolution can be achieved with the minimal contribution from background radiation. Although non-dispersive systems have been used, dispersive systems currently find greater applicability.

Since 1950, the range of detectable elements has steadily increased:

1950 $Na \rightarrow U$	1960 $C \rightarrow U$	1965 $B \rightarrow U$
1967 $Be \rightarrow U$	1968 $Li \rightarrow U$	

An idea of the performance of different crystals can be gained from *Figure 4*. It can be seen that with only 5 different crystals, more than 90 per cent of the known elements can be covered. Today nearly every instrument has 2–3 spectrometer units with a range of 6–8 crystals. In analyses for lithium, gratings rather than crystals are at present being investigated.

Limits of detection

The question of the lowest amount of a particular element which can be detected or determined cannot be answered in a general way, since the matrix,
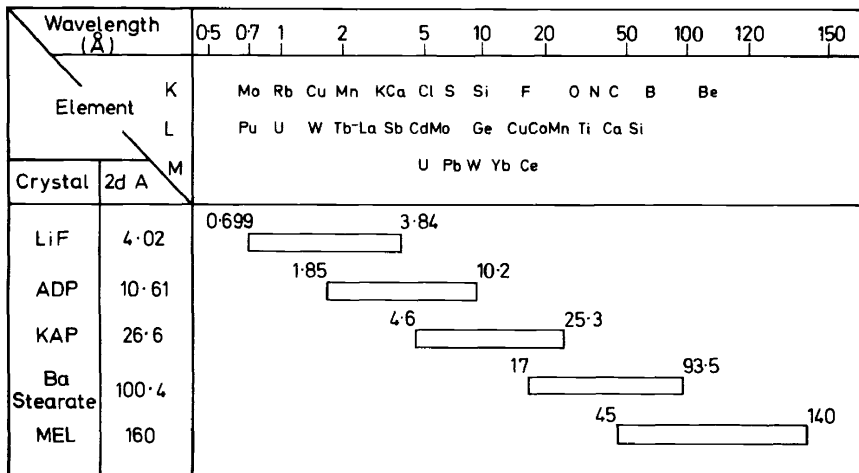
Figure 4. Spectrometer wavelength coverage. ADP, ammonium dihydrogen phosphate; KAP, potassium hydrogen phthalate; MEL, Melissat

Table 5. A comparison of limits of detection for pure elements

	1960	1964	1968
Cr	6×10^{-9}		
Mn	4×10^{-9}		
Fe	1×10^{-9}		
Co	7×10^{-10}		
Ni	5×10^{-10}		
Cu	4×10^{-10}	3×10^{-14}	6×10^{-16}
Zn	4×10^{-10}		
Sr	2×10^{-9}		
Mo	7×10^{-9}	9×10^{-14}	
W	5×10^{-9}	9×10^{-14}	
Au	8×10^{-9}	2×10^{-13}	
Al	6×10^{-8}	2×10^{-14}	

Table 6. Limits of detection for various elements in steel

Element	Limit of detection (%)	Concentration in sample (%)
Si Kα	0·053	1·20
P Kα	0·029	15·6
S Kα	0·029	—
Cr Kα$_1$	0·019	1·17
Mn Kα$_1$	0·015	0·27
Co Kα$_1$	0·016	0·23
Ni Kα$_1$	0·014	1·23
Cu Kα$_1$	0·014	0·12
Mo Lα$_1$	0·089	1·49

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the homogeneity of the matrix and the preparation of the surface for analysis all play important rôles in governing the limits of detection.

If analysis of the pure elements is carried out, a reasonably valid comparison can be obtained for guidance, as shown in *Table 5*. However, for the purpose of chemical analysis, it is much more important to know the lowest concentration of element A that can be detected or determined in matrix B. As an example, the limits of detection found for various elements in steel are shown in *Table 6*; these limits were established under the optimal conditions of accelerating voltage for each element concerned[8].

It seems that there are now very few analytical problems that cannot be solved by means of electron probe microanalysis, always provided that a solid sample is available. Tousimis and Adler[9], in 1963, investigated the content and distribution of copper in the cornea of the human eye, and since that time, investigations of living specimens, vein walls, bones, etc. have become routine in universities and hospitals. Oxidic materials such as dolomites, limes and silicates can now be analysed, as well as carbides, sulphides, borides, etc., in metallic samples. Nearly every branch of science has found benefits from the introduction of this technique.

INTERACTION BETWEEN ELECTRON BEAM AND SAMPLE: QUANTITATIVE ASPECTS

For a proper understanding of the difficulties that can be encountered in electron probe analysis, particularly in quantitative work, it is necessary to look closely at the interaction of the electrons with the different elements in the sample.

In the analysis, electrons accelerated to an energy in the range of 5–50 kV are focused on the sample, usually to a diameter of 1μm, carrying a current between 1 μA and 1nA. This beam strikes the specimen at the point to be analyzed. The interaction of the electrons with the atoms in the sample can be classified into two parts: (a) elastic scattering in which there is a considerable change of direction so that the result may be the backscattered electrons; (b) inelastic interaction which leads, not in every case but very often, to the ionization of an inner electron shell producing K or L characteristic x-ray quanta.

The interaction can be of considerable complexity (cf. *Figure 2*), and the atomic number correction can be very difficult to establish. All the models that have been proposed are, to a greater or lesser extent, simplifications. Even treatments of the problem by means of Monte-Carlo procedures and computer techniques are not entirely satisfactory.

Corrections necessary for quantitative analysis

In his Thesis, Castaing[10] stated that, as a first approximation, the concentration of an element A is equal to the ratio of ionization in the sample and the standard. Thus:

$$c_A = n_{A_s}/n_{A_{st}}$$

or, in terms of the measurable intensity, I_{A_s}, of the characteristic radiation of

element A in the sample, and the intensity, $I_{A_{st}}$, of the same radiation of the pure element under identical conditions:

$$c_A = I_{A_s}/I_{A_{st}}$$

Very often this simple equation can be used successfully, especially if the sample and standard are very similar. However, there are also many deviations from this approximation, so that corrections become necessary. The corrections required and the reasons for them may be summarized as follows.

1. If elements of widely differing atomic number are present, the intensity of the characteristic x-rays generated within the sample is not proportional to the concentration. This necessitates a correction for the so-called *atomic number effect* (F_1).

2. The x-rays are generated below the surface of the sample and thus they must be partly absorbed by the matrix as they emerge from the sample. This is the reason for a further correction parameter for the *absorption effect* (F_2).
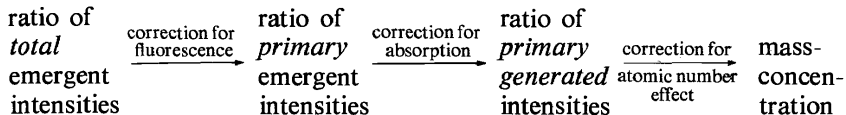
3. As the initially produced x-rays travel through the sample they can, under certain circumstances, generate further radiation; this leads to an enhancement of the total radiation, hence a third correction must be made, *the fluorescence correction* (F_3).

When these corrections are included, we have

$$I_{A_s}/I_{A_{st}} = k_A = c_A \cdot F_1 \cdot F_2 \cdot F_3$$

where k_A is the measurable ratio of intensities.

According to Philibert and Tixier[11] a possible scheme of calculation is as follows:

ratio of total emergent intensities	correction for fluorescence →	ratio of primary emergent intensities	correction for absorption →	ratio of primary generated intensities	correction for atomic number effect →	mass-concentration

The secondary emissions have to be subtracted from the total measured intensities and the resulting primary emergent intensities have then to be corrected for the absorption effect; finally the true concentration is calculated from the ratio of the primary generated intensities, after correction for the atomic number effect. However, the situation with regard to the correction factors is in dispute, and the methods of computation are still under development. The unsatisfactory nature of the present understanding of these factors is well illustrated by the fact that about 17 different formulae for correction are currently in use. Mulvey[12] has recently pointed out:

'The general physical picture of the interaction of the electron beam with the specimen in the x-ray microanalysis is clear. Nevertheless, many of the numerical results yielded by even the most successful theoretical calculations fall outside the range of experimental error. An improvement in this position can be attained in principle, but only at the expense of long and tedious calculations. However, if one is prepared to limit the field of application of a model on an empirical basis *or* introduce plausible assumptions, surprisingly accurate quantitative analysis can be performed in practice.'

The above description served to indicate why it has become more common to prepare standards which simulate the samples as far as possible, rather than

to use the pure elements; preparation of suitable standards is of extreme importance in view of the difficulties encountered in the application of formulae derived from a theoretical physical standpoint.

These difficulties arise from a variety of causes in addition to those mentioned above. For example, there is still no proper agreement on mass-attenuation factors and this would appear to be a proper task for IUPAC. Another cause involves the 'analysed volume' of the sample. According to Castaing[10], the analysed volume depends on the diameter of the beam, d_s, and

Table 7. Penetration depth for an accelerating voltage of 20 kV.

Compound	Mean atomic or molecular weight	Mean atomic number	Density	Penetration depth (μm)
U	238	92	18·7	0·67
Mg	24·3	12	1·74	6·2
Ca	40·08	20	1·55	6·3
CaO	56·1	14	3·4	3·2
MgO	40·3	10	3·6	3·0
2 MgO. SiO$_2$	140·7	10	3·2	3·4
MgO. Fe$_2$O$_3$	200	13·7	4·5	2·6
2 CaO. SiO$_2$	172·3	12·3	3·3	3·3
CaO. Fe$_2$O$_3$	271·9	14·7	4·5	3·2
CaO. MgO. SiO$_2$	156·5	11·1	3·2	3·4
MgO. Al$_2$O$_3$	142·3	10	3·6	3·1
3 CaO. MgO. SiO$_2$	328·8	12·2	3·2	3·4
SiO$_2$	60·1	10	2·3	4·7
Al$_2$O$_3$	101·9	10	3·7	3·0

on the depth of penetration, d_E, of the electrons. The depth of penetration can be calculated as described by Wittry[13]. For metallic samples, the so-called analysed volume is 2–5μm for acceleration voltages of 20–30 kV and a beam diameter of about 1μm. But for non-metallic systems with relatively low average atomic numbers, an entirely different situation obtains; the depth of penetration may be as much as 30–40 μm for an acceleration voltage of only 20 kV. Since the production of x-rays takes place in at least the 'analysed volume', it is essential, even with a very fine electron beam, that the grain size of the phases which compose the sample should be large enough to comprise the entire 'analysed volume'.

During the past ten years it has been found that, for practical purposes, with few exceptions, changes in the beam diameter below 1 μm do not have a very significant effect, and the resolving power does not improve if the diameter of the beam is reduced, as is possible, down to 0·1 μm. In the ordinary x-ray technique, the general tendency is to use an accelerating voltage for the electron beam equal to at least three times the critical excitation voltage of the x-level. If this rule is maintained in x-ray microanalysis, the accelerating voltage that has to be used for assaying copper, for instance, is of the order of 30 kV. Under such conditions, the diameter of the irradiated region of the sample is greater by about 2 μm than the actual diameter of the electron probe, and there would be

little point in seeking to improve the resolving power by reducing the diameter of the probe below 0.5 µm.

To reduce the diameter of the probe and of the irradiated sample area further, it would be necessary to use very low accelerating voltages, just above the critical excitation voltage, and the analysis would then be restricted to the very first layers of the sample. However, under such conditions, technical difficulties would arise from the weakness of the characteristic lines and from the sensitivity of the analysis to impurities in surface films arising from contamination.

Another difficulty is caused by the fact that a mean atomic number is used in the calculations. This means, for example, that calcium ferrate should show the same 'behaviour' as potassium which is certainly not the case.

Errors caused by grain size, orientation and inhomogeneity

A further problem may be created by a lack in uniformity of grain size, and, also very important, in orientation of the grains. This means that the 'analysed volume' may consist of a heterogeneous system, so that incorrect results may occur. *Figure 5* shows a typical case schematically. With an optical micro-
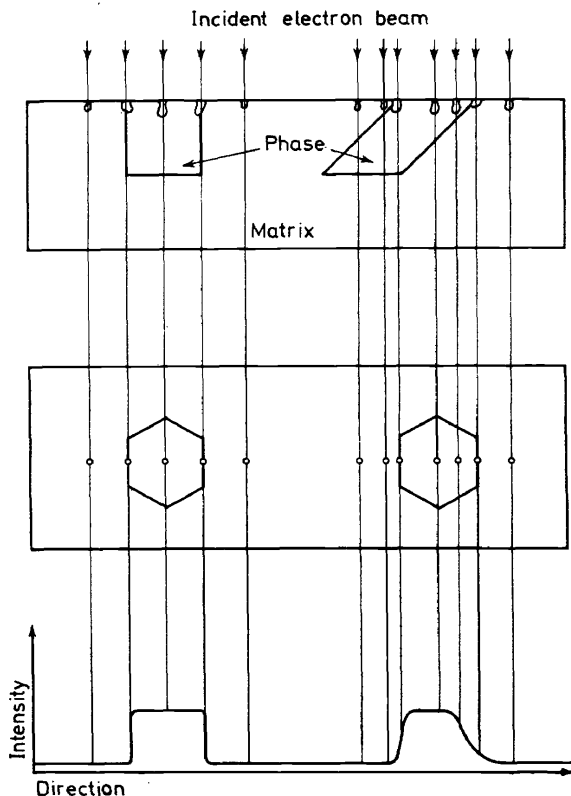

Figure 5. Errors caused by variable orientation of sample grains

scope only the surface can be viewed, and it is impossible to predict how the orientation of the crystal continues with depth. This type of error can be at least as serious as the choice of the proper correction formula. If the crystal or phase is truly vertical to the surface, then a concentration profile such as that shown on the left-hand side of *Figure 5* is obtained, but if the orientation is oblique, then the profile appears as on the right-hand side.

Even if perfect correction formulae were available, some invisible part of the region located under the free surface, may show important changes in its chemical constitution. A precipitate, for instance, may occur just below the analysed point in a region which the electrons cannot reach, and a large error in a quantitative analysis will then be obtained; it is impossible to correct for such errors even approximately. In contrast to what happens for the self-absorption correction, the trouble in this case arises from an unknown part of the specimen, and a certain amount of 'fluorescence uncertainty' is bound to remain. This uncertainty could be reduced by using very small values for the
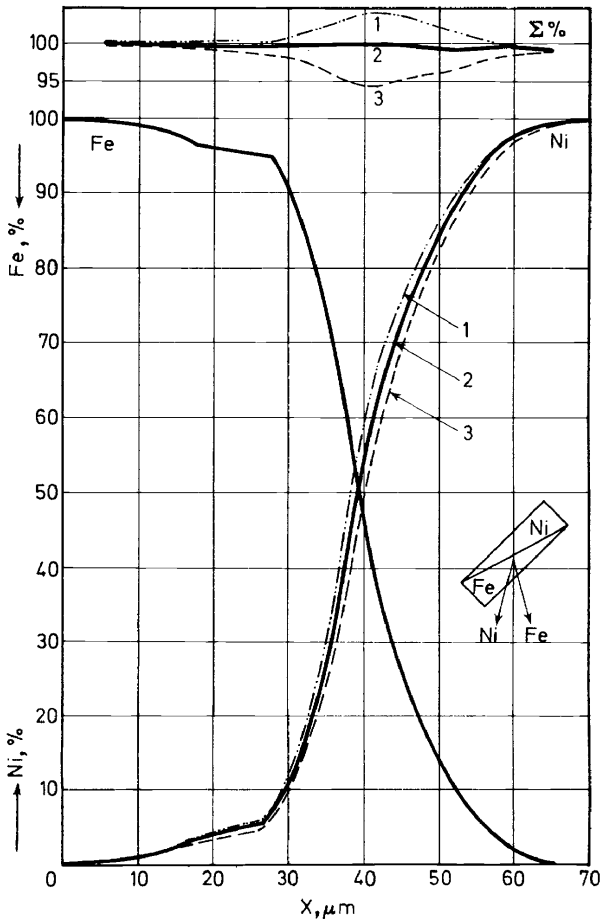

Figure 6. Diffusion curves for nickel and iron. (Heating at 800° for 48 h)

angle of emergence of the x-ray beam, for in such a case the fluorescence emission of the deep layers is eliminated by self-absorption; but difficulties would occur in the analysis of specimens whose surface is not perfectly flat.

It must be borne in mind that all correction formulas are valid only for a homogeneous matrix in view of x-ray production. This means that the irradiated volume must contain the same concentration of the element that is being determined, as that part of the specimen through which the x-rays travel to reach the detectors. This aspect of the electron probe makes it clear why a high take-off angle is generally preferred. As a compromise, most instruments have a take-off angle between 30 and 60°.

If diffusion problems or the composition of inclusions or reaction products which have a broad solubility band are to be studied, the calculation of the concentration is different in principle. In the usual calculation, as discussed by Philibert, it is assumed that the radiation which is produced in the irradiated volume travels through areas of identical composition on its way to the detectors, undergoing some absorption; in this case,

$$c_A = k_A \cdot \frac{1}{F_{abs}}$$

If there is a gradient in concentration this formula is not applicable. However, it has proved possible to develop a useful formula for such conditions[14]:

$$c_A = k_A \cdot \frac{1}{F'} K$$

In the first formula, F is a constant, whereas in the latter case both F', and K are functions depending on the gradient of the change in concentration. The value of this new formula can best be demonstrated from *Figure 6* where the diffusion curves of nickel and iron are shown. If the calculations are made by means of the first approximation of Castaing, then the sums of nickel and iron obtained are too high, by up to 5–6 per cent (curve 1), and if the absorption correction of Philibert is applied, then the sums are low to about the same extent (curve 3); only with the new formula can good agreement be achieved (curve 2)[14].

APPLICATIONS OF ELECTRON PROBE MICROANALYSIS

For some years now electron probe microanalysers have been used routinely in several different ways. For point analyses, the beam is exactly adjusted on a previously selected point of the surface of the specimen. Today this is still the most accurate method for quantitative analyses, because all the essential conditions and parameters can be fulfilled (the Rowland conditions, etc.)

Scanning methods

Every commercial instrument allows three different kinds of scanning. *Bragg angle scanning* is used primarily for the qualitative identification of elements. There are two main possibilities in *beam scanning*. The beam can be scanned over a small area by electrical deflection. The signals from the x-ray or electron detector are used to modulate the intensity of the cathode-ray tube, which is synchronised with the scanning speed of the probe. With this arrangement, it is

possible to obtain a very good picture of the distribution of elements in the area covered, but this procedure cannot be used for exact quantitative measurements, because the Rowland circle conditions are fulfilled only over a very small area.

The second possibility in the use of electronic scanning is to deflect the probe along a line and to record the distribution of the element of interest along this line. This method of line scanning is very fast but gives only semiquantitative results. One of the reasons is that the electron beam does not remain long enough at any one point for the full intensities to be generated.

In another method, so-called *mechanical scanning* is employed. In this case the probe remains stationary and the specimen is moved more or less slowly under the probe. Here the Rowland conditions can be fulfilled strictly, and the results can be evaluated almost perfectly, especially if the scanning is carried out stepwise so that the conditions are essentially the same as in point analyses. This type of procedure is very close to the Moseley arrangement.

Table 8. Precision of point measurements, indicated by analysis of the matrix and the boride in a steel containing 4·7 per cent boron

	Matrix		Boride	
	%†	S	%	S
Cr	11·3	±0·7	62·0	±1·0
Fe	61·0	±1·0	27·0	±1·0
Ni	21·4	±0·6	1·0	±0·04
Mn	0·99	±0·07	0·54	±0·02

† Mean of 10 determinations at different positions.

The precision of point measurements is illustrated in *Table 8* which summarizes the analytical results obtained for four elements in the matrix and in the boride inclusions of a steel containing 4·7 per cent of boron. It is of interest to note that both the primary boride and the boride-free part of the eutectic matrix appear to be completely homogeneous phases. The precision of these analyses is remarkably good considering that none of the boride inclusions was thicker than 20 µm.

Studies of electrode behaviour

There are so many notable examples from metallurgy and other disciplines that it is impossible to give even a reasonably full survey of the manifold applications of electron probe microanalysis. The following example is of interest in that it indicates the fruitfulness of combining chemical and electron probe methods. The problem concerned the determination of traces of copper in solution[15]. The electrodeposition of copper from certain electrolytes gave a good mirror-like surface which was of even thickness. Measurements with the electron microprobe, however, showed that there was a perceptible rim on the electrode (a 5-mm platinum disc) where the deposit was thicker, although this was not such as to affect the usefulness of the procedure. This initial finding may later lead to further studies of the reaction mechanisms on electrodes.

Recoveries of copper on the 10-μg scale were about 90 per cent from solution to electrode.

Small, known quantities of copper were deposited on the electrodes by means of constant-current coulometry, and these samples were measured in the electron probe microanalyser. Multiple counts on several different points on each electrode were made in order to obtain a measure of the mean thickness and of its variation. The layers were then stripped and the copper was determined spectrophotometrically, as a final check. Very good linearity between count-rates and the amount of copper was found for the range up to 35 μg, corresponding to a thickness of 0·2 μm. Measurements were possible up to a thickness of about 0·5 μm. Total recoveries of 80–90 per cent were obtained and the mean result obtained on 10 counts per sample, all on different points of the electrode surface, was 30 μg with a standard deviation of 10·6 μg. The time required for collection, electrolysis, and measuring was approximately 30 minutes for each analysis.

Very recently, Meites and Chodos[16] used electron probe microanalysis to investigate the oxide films of platinum–iridium electrodes. Even in only preliminary tests, these workers found that there is some evidence that can be taken as implying the chemical participation of oxide films in electron-transfer processes at noble metal electrodes. As the redox behaviours of iridium and platinum are quite different, the slow accumulation of iridium—either as an impurity or as an added alloying element—might well alter the electrochemical behaviour of an electrode. No doubt this behaviour would also occur with many other elements, and it may be guessed that this phenomenon may be at least partly responsible for the familiar dependance of the properties of a platinum electrode on its previous history.

Stereometric analysis

Another combination is the use of a so-called 'phase integrator'[17] with an electron probe microanalyser, the aim being to develop a real stereometric, *i.e.* three-dimensional, analysis. The electron microprobe has proved to be a very valuable tool for the determination of the chemical composition of phases and it has nearly the same spatial resolution as the light microscope. The instrument, therefore, lends itself readily to applications in the field of stereometric analysis, especially since the scanning microprobe design offers the possibility of scanning the sample in straight lines. Thus, the most sophisticated method of stereometric analysis, linear analysis, can also be accomplished with the microprobe. It is not surprising that several attempts in this direction have been made independently by different investigators. At the same time as Dörfler and Plöckinger[17] discussed their phase integrator, Melford and Whittington[18] described the development of an 'inclusion counter' which is based mainly on a computer technique. This counter analyses the x-ray and backscatter output of the microprobe. The phases or inclusions are distinguished by the presence or absence of the elements in question, and by the value of the mean atomic number as given by the intensity of the backscattered electrons. If a phase is identified, sizing circuits are activated, which record the number of intercepts falling into a special size class. A special provision is made to avoid the counting of an inclusion twice while analysing on subsequent lines. This

method is extraordinarily rapid, the analysis on a field of 500×500 μm^2 being performed in 30–60 seconds.

The basic principle of the apparatus known as a 'phase integrator' is as follows. A signal of the electron microprobe (x-ray, target current, etc.) is fed into a discriminator circuit, where the identification of the selected phase is accomplished. If the signal voltage remains within the lower and upper threshold limits, a constant voltage is applied which opens a gate. Through the open gate, pulses of constant frequency, which are produced by an external oscillator, can pass to the analysing circuits. The pulse groups obtained in this way represent the intercept length of the linear analysis and can, therefore, be analysed to give all the structural parameters required.

For routine use, the coupling of computers with analytical techniques such as electron probe microanalysis which yield their data in the form of high impulse rates, is of very great importance, and in the future such combinations will become essential. Because of the high count rates involved and because of the complex nature of the many parameters required for quantitative evaluation, *e.g.* atomic number correction, specially designed computer programmes have recently been developed[19].

CONCLUSION

At the present time, the instrumentation available for electron probe microanalysis has reached a very high standard of performance, and its handling is as straightforward as is likely to be achieved. The method offers very great possibilities to analytical chemistry both alone and in combination with other methods; indeed, there are few branches of science to which the application of electron probes cannot bring new and valuable results that could not be achieved by other means.

At the present time, there is a considerable discrepancy between the very rapid production of the signals and their very slow evaluation, but as electron probe systems become fitted with on-line computers, this problem will disappear. The technique is one of those which are particularly adaptable for automation and work on these lines is proceeding rapidly in many places.

Many basic problems remain unsolved; for example, the distribution of the characteristic x-rays produced in the sample volume. In 1968, Mulvey[12] stated that 'it is at this level that the real difficulties begin'. He surely meant the solution of analytical problems by means of pure mathematics. However, such problems can be obviated provided that suitable standard samples are available, and in routine work, the great majority of analytical questions can be solved without difficulty.

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