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Quantitative Electron Probe Microanalysis of Ultralight Elements (Boron-Oxygen)

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Introduction

Due to the rapid development and expansion of materials science into new areas such as high-temperature materials, wear-resistant coatings, and modern ceramics, interest in quantitative electron probe microanalysis of ultralight elements, such as B, C, N, and O, elements which are usually present in considerable quantities in such materials, is also rapidly growing. Compared with conventional analysis of medium-to-high Z elements ($Z > 11$), successful analysis of ultralight elements requires far more stringent adherence to all of the steps involved in the complete procedure; beginning with the specimen preparation, followed by the actual intensity measurement, and ending with the matrix correction.

As far as specimen preparation and intensity measurements are concerned, a number of specific problems have already been discussed at length (Bastin and Heijligers 1984a, b, 1986a-c), the major problem being the very low count rates and frequently low peak to background ratios, especially for an element like nitrogen. There is also a theoretical possibility that x-ray emission for ultralight elements may exhibit systematic differences from one compound to another. Evidence to this effect has recently been found, for example, for B-

$K\alpha$ in Ni-compounds (Bastin and Heijligers 1986b, c). Additional practical problems such as a lack of electrical conductivity which can strongly affect the intensity measurements, are gradually being recognized. Regarding matrix correction, necessary in order to convert the measured intensity ratios (k -ratios) into concentrations, the corrections for ultralight elements can be an order of magnitude larger than in conventional analysis. The demands imposed upon a specific matrix correction program are correspondingly far reaching. Furthermore, it is vital that certain physical quantities such as, for example, mass absorption coefficients (MACs) are available with an accuracy of $\pm 1\%$ relative. Unfortunately, it is highly unlikely that such values are actually available with the required precision, considering the practical difficulties involved in the measurement (or calculation) of these quantities. In light of these uncertainties, it is almost impossible to make definite statements on the performance of correction programs, especially on their correction for absorption. This would be possible only if large databases were available for each of the light elements. Once such data are available they can be used in an iterative process to test various programs in conjunction with various sets of published MACs. A next iteration step could provide improved equations in a specific program and/or an improvement in the consistency of the MACs used. Ultimately, a good program can be used to test the consistency of the MAC values.

The first important step is the collection of good light-element data for a wide range of compounds and accelerating voltages and our laboratory has been very active in this field since 1983. Work on carbon, boron, and nitrogen has been completed (Bastin and Heijligers 1984a, b, 1986a-c) and the work on oxygen is in progress.

Fortunately, considerable improvements in microanalysis have been realized in the last decade, on both the hardware as well as on the software side, which will make life much easier for the microanalyst attempting

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to do quantitative EPMA of ultralight elements. A very important step forward is the introduction of the new synthetic multilayer crystals which can produce 2–15 times higher peak intensities and usually suppress higher-order reflections very strongly, thus reducing the problems of background determination considerably. Equally important is the strong progress in matrix correction programs that has been realized in the past ten years, especially in the introduction of the so-called $\phi(\rho z)$ programs (Bastin *et al.* 1984a, Packwood and Brown 1981, Pouchou and Pichoir 1984). Because these programs are based on attempts to describe as accurately as possible the number of ionizations or x-ray photons (ϕ) as a function of the mass depth (ρz) in the specimen, they must be considered as the most direct, genuine, and straightforward approach to bulk matrix correction. They also provide the best possible basis for thin-film analysis and in-depth profiling procedures.

New Synthetic Multilayers

The introduction of commercially available (e.g., Ovonic Corp., Troy, MI) synthetic multilayer crystals has brought considerable improvements in the analysis of ultralight elements. These improvements consist of a significant increase in the peak count rates for light elements. The sometimes strong suppression of higher-order reflections, which are usually a big nuisance in the background determination, is in our opinion at least as important. At present, our microprobe (JEOL 733, 4 W.D.-spectrometers + EDX system) is equipped with two such new crystals, in addition to our conventional Pb-stearate crystal. The first, (LDE), consists of 200 pairs of alternating W (less than 10 Å) and Si (several tens of Å) layers, 2d-spacing 59.8 Å, and has been specially designed for the analysis of N, O, and F. The second, OVH, is a Mo/B₄C multilayer, 2d = 149.8 Å, optimized for B and Be. These crystals have been extensively tested and their performance compared with that of the conventional stearate (STE) crystal. The quantitative work on oxygen is almost exclusively being done with the LDE crystal. The work on nitrogen has been done with both STE and LDE crystals simultaneously, which makes a straightforward comparison under identical circumstances easy.

Figure 1 compares typical performance of the LDE crystal with that of the STE crystal. The increase in the peak count rate is obvious; perhaps even more important is that the remnants of higher-order Zr reflections on the STE crystal are completely suppressed on the LDE crystal, thus yielding a smooth background which is extremely important in view of the low peak-to-background ratios. An impressive example of the sensitivity of the LDE crystal for O-K α is given in Figure 2 where an oxygen peak could be recorded on pure gold.

As a matter of fact, an oxygen peak can be found on virtually all elemental standards with the LDE crystal. This shows how surface sensitive a microprobe can be, since the solid solubility of oxygen in gold is negligible.

Figure 3 gives an example of the performance of the OVH crystal. The huge increase in peak count rate on the OVH crystal now offers the possibility to measure B-K α X-rays under the same conditions (15 keV, 10 nA) which are normally used for much heavier element radiations such as Cu-K α , thereby greatly improving the compatibility of conditions optimal for light element radiations with those for heavier element radiations. Normally, such cases require conflicting conditions in terms of, for example, beam current in order to avoid excessive dead-time corrections. An interesting feature of the OVH crystal is that its possibilities extend toward Be-K α , an element which so far could only be measured (with very low count rates) with a lead-cerotate crystal. A more than 20-fold increase in the count rate has been realized here.

A typical advantage of the new multilayers, which has so far hardly been discussed in the literature, is that they are much less sensitive to peak shape alterations in the light element x-ray emission peaks compared with the conventional Pb-stearate crystal. This must be attributed to the somewhat poorer resolution of these crystals (see e.g., Fig. 3). These peak shape alterations, which are, in fact, one of the biggest problems in the quantitative analysis of ultralight elements, are discussed below.

Peak Shape Alterations

In electron-probe microanalysis, it has always been common practice to measure the intensities of peaks at the spectrometer settings with the maximum count rates. It is usually not realized that, in principle, integral intensities are required. Peak measurements are correct only under the tacit assumption that the peak intensity is proportional to the integral emitted intensity. Fortunately this assumption is correct for the K- and L-radiations of medium to high Z-elements.

However, for ultralight element radiations, this assumption is no longer justified as Figure 4 shows, and peak measurements, even when peak shifts are taken into account, can and will lead to large errors (Bastin and Heijligers 1984a, b, 1986a, b). In order to elucidate this effect, the net C-K- α peak intensities emitted by glassy carbon and TiC have been scaled to the same value; which would yield a peak k-ratio of 1. One glance at Figure 4, however, shows that this approach cannot be correct because it does not show that the peak emitted by glassy carbon is approximately twice as broad as that from TiC. Thus, the true k-ratio for TiC, relative to glassy carbon, should rather be 0.5 and not 1.0. It will immediately be clear that, in this particular case, an

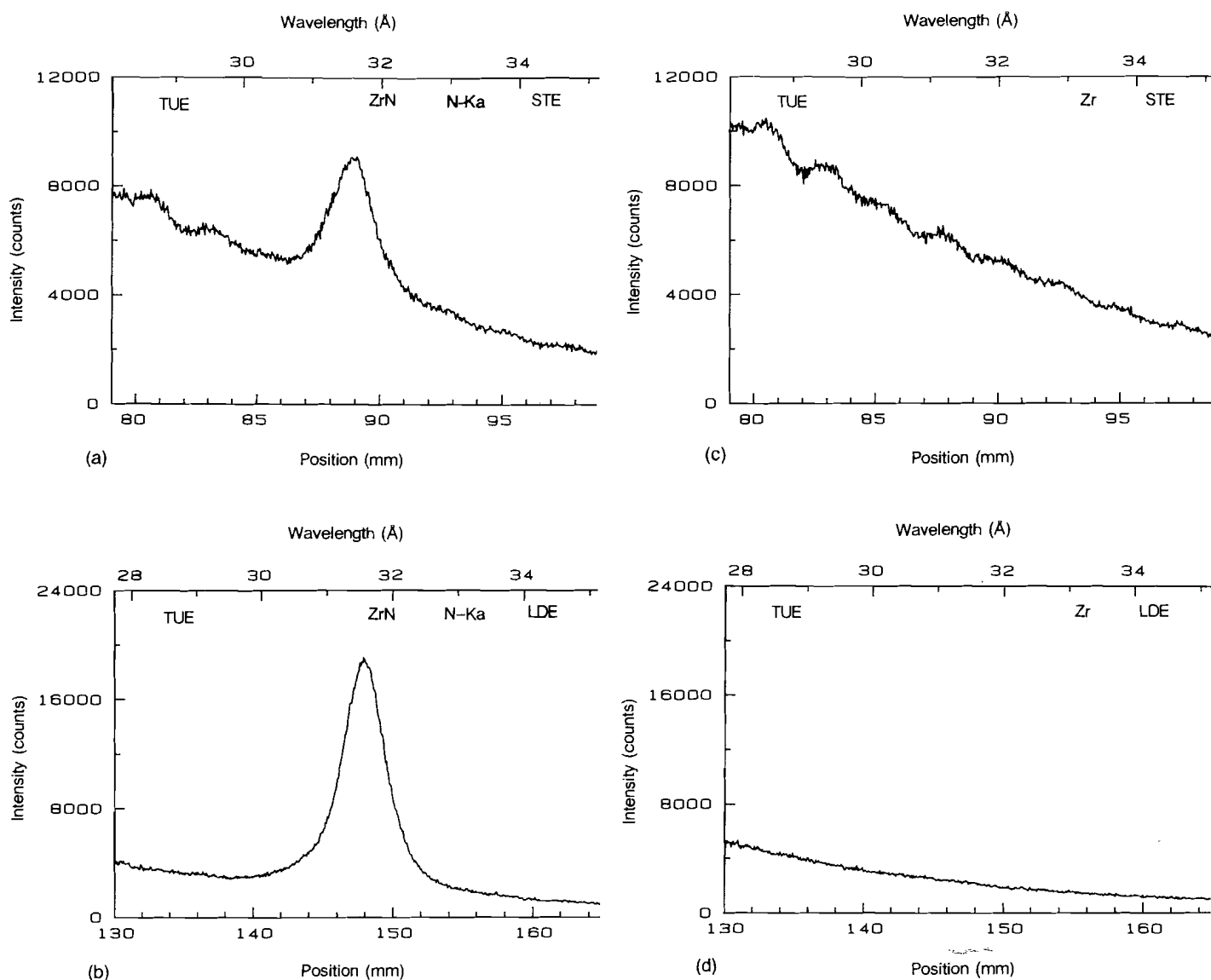


FIG. 1 Nitrogen spectra recorded from ZrN with conventional STE crystal (a) and new LDE crystal (b); (c) and (d) gives backgrounds from elemental zirconium. Exp. conditions: 10 keV, 300 nA. Note the difference in the vertical scale for LDE vs. STE of a factor of 2.

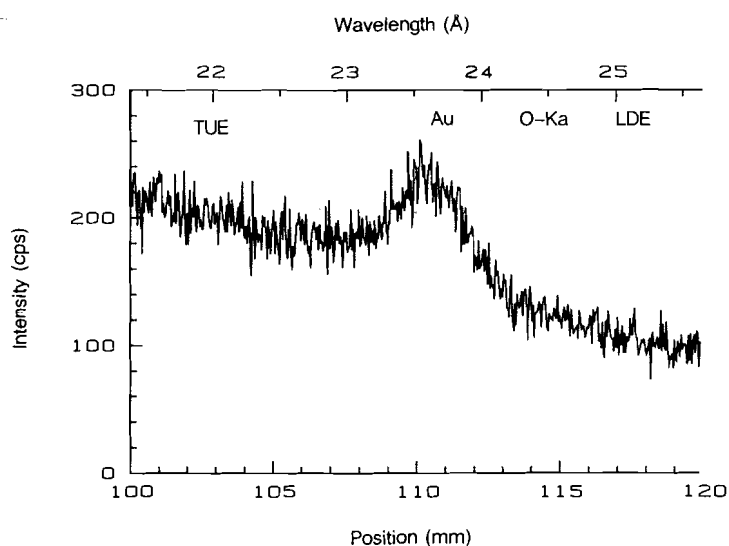


FIG. 2 Oxygen peak recorded on pure gold with the LDE crystal. Exp. conditions: 10 keV, 50 nA.

error of 50% can be made when the effects of peak shape alterations are neglected, an error which can never be rectified afterwards.

For boron, almost the lightest element which can be measured in the electron probe microanalyzer, the situation is even more complex.

Apart from the peak shifts and peak shape alterations which are, of course, to be expected, two new complications turn up: (1) The peak position in a specific boride can vary strongly from one crystal in the specimen to another and is apparently strongly dependent on the crystallographic orientation of the specimen. (2) The peak shapes vary with the peak shifts.

To give an idea about the magnitude of these effects: Typical peak shifts can be of the order of 1 mm (0.357 Å) and the associated variation in peak shape is best demonstrated with the aid of Figure 5.

The broadest peak is always found at the longest wavelength and the narrowest one at the shortest wavelength. This particular effect can be observed even in one single crystal of the specimen, merely by rotating it in its own plane under the electron beam. The boron peak will shift back and forth during this rotation and at the same time it will change its shape continuously. This peculiar phenomenon is not unlike the effects observed when viewing a specimen under a microscope with crossed polars while rotating the specimen table. In fact, the origin of both phenomena is the same: the peak shape alterations in the B-K α peak are caused by the presence of polarized components (Wiech 1981) in the emitted radiation and the filtering action that can be exercised on specific components by the Pb-stearate crystal under certain conditions.

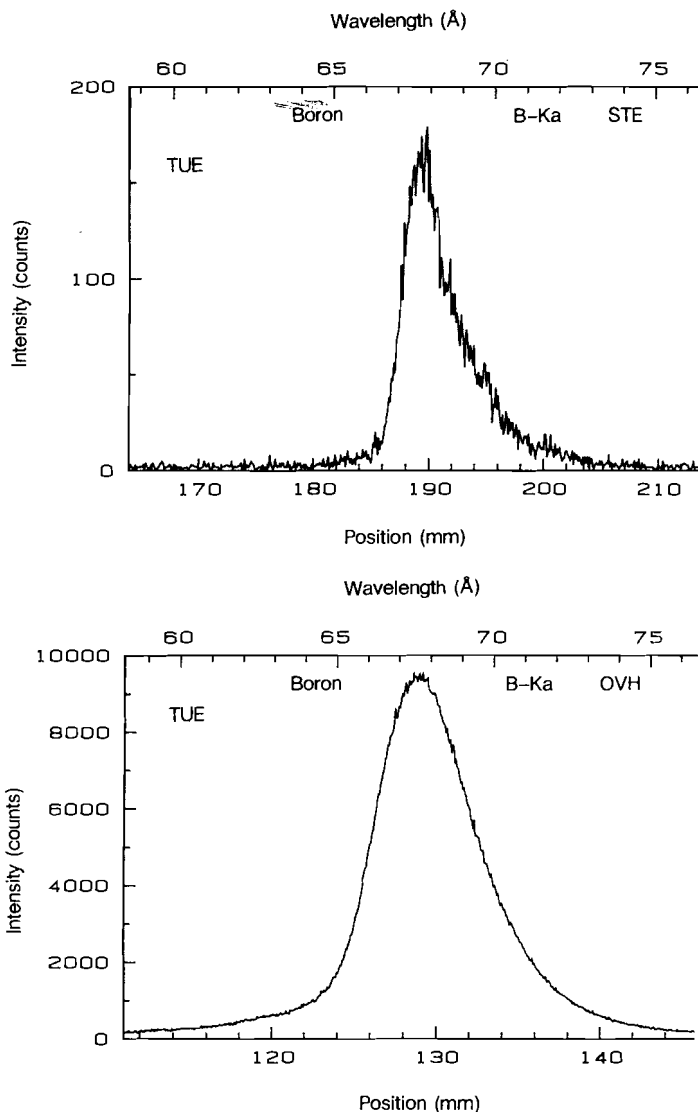


FIG. 3 Performance of the OVH multilayer ($\text{Mo}/\text{B}_4\text{C}$) as compared to that of the conventional stearate crystal for B-K α x-rays, emitted from elemental boron. Note the difference in the vertical scale for OVH vs. STE of a factor of 50. Exp. conditions: 15keV, 10 nA.

This effect can, in principle, be expected in all compounds with a crystal symmetry lower than cubic and higher than triclinic. Polarization takes place (see Fig. 6) in two mutually perpendicular planes (PI and PII) which are aligned along the principal crystallographic directions of the crystal lattice. As it turns out, the filtering action of the analyzer crystal is optimal when the angle of incidence of the x-rays on the crystal equals 45°. In our spectrometer this angle happens to be 42.5° for B-K α , which is very close to the optimum angle.

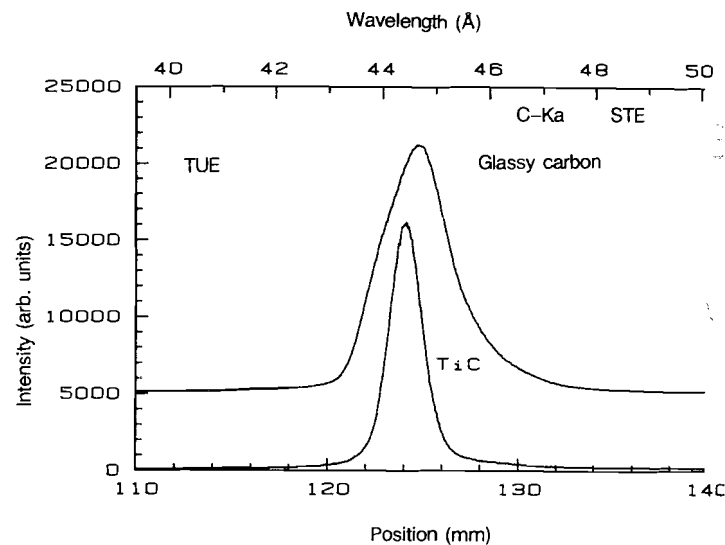


FIG. 4 Carbon-K α emission profiles recorded from glassy carbon and TiC at 10 keV and 300 nA (stearate crystal). Spectra have been scaled to yield the same net peak count rates. Note the peak shift and the extreme peak shape alteration.

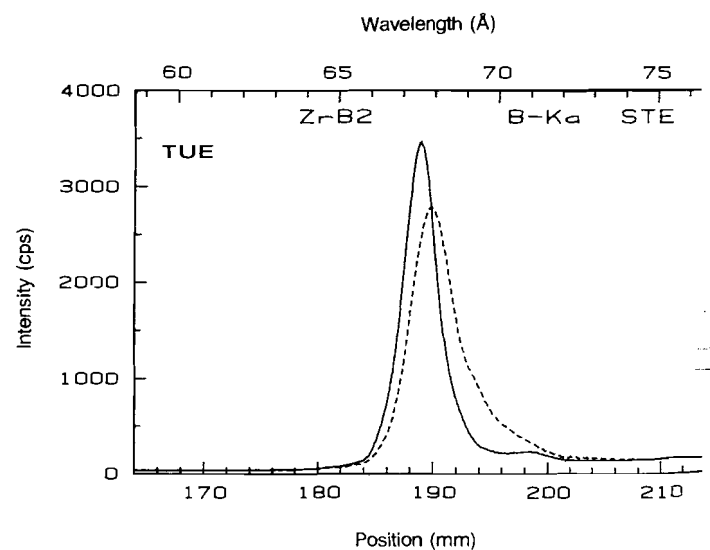


FIG. 5 The two extremes in the peak shapes of the B-K α spectrum emitted by ZrB_2 . Exp. conditions: 10 keV, 300 nA, stearate crystal.

The most pronounced shape alteration effects have so far been found in hexagonal compounds like TiB_2 and ZrB_2 . As expected, the relatively few cubic borides did not show an orientation-dependence of the peak shape and peak position.

Approximately 50% of the 28 investigated borides (and also elemental boron) did not exhibit this effect although, from a theoretical point of view, it could be present. This does not mean, however, that such borides can be measured on the peak. As Figure 7 shows there are still large differences in peak shapes which have to be taken into account. A striking example in this context is the spectrum emitted by hexagonal BN: The two satellites on both sides of the main peak actually belong to the integral $B-K\alpha$ spectrum and as such, their intensities have to be included in the measurements. The $B-K\alpha$ spectrum emitted by cubic BN showed that the left-hand satellite was almost gone; the integral intensity, however, was exactly the same.

Large errors in the intensity measurements can obviously be made when peak shape alterations are ignored.

In the case of boron, these errors can be made even when the same compound is used as a standard. The

variations in peak intensity can be in the order of several tens of percent merely due to the influence of the crystallographic orientation (see Fig. 5).

The effects discussed here are worst for the lightest element boron and slightly less bad for carbon, where at least the crystallographic effects and polarization phenomena are absent. For nitrogen and oxygen the effects of shape alterations decrease rapidly. In the latter case the effect is hardly noticeable, at least for the LDE crystal. The microanalyst trying to deal with ultralight elements has to be constantly aware of peak shape alteration effects, and the lighter the element, the more caution should be exercised. In the majority of cases, it is simply imperative to perform the intensity measurements in an integral fashion, which is a very frustrating prospect for on-line analysis with a wavelength-dispersive spectrometer.

A considerable reduction in time and effort can be obtained by the use of the area-peak factor concept (Bastin and Heijligers 1984a, b, 1986a-c), which is discussed in the next section.

The Area-Peak Factor Concept and Its Use

The area-peak factor (APF) has been defined as the ratio between the correct integral (or area) k-ratio and the peak k-ratio. It should be clear from the beginning that this factor is only valid for a given compound with respect to a given standard and for a given spectrometer with its own typical resolution.

Once an APF has been determined, future measurements on the compound in question can simply be carried out on the peak again; subsequent multiplication of the peak k-ratio with the APF will then yield the correct integral k-ratio.

To a large extent, the APF can be regarded as a relative width-to-height ratio (relative to the standard) or also as a kind of weight factor which has to be assigned to a certain peak intensity. It should certainly not be confused, however, with the full width at half maximum (FWHM) of the peak because in the vast majority of cases peak broadening takes place at the foot of the peak and, as a consequence, the FWHM value is usually relatively insensitive to this effect.

Furthermore, it must be clear that APF values measured on one particular microprobe cannot blindly be transferred to another one because the APF is strongly related to the resolution of the analyzer crystal and spectrometer.

The only quantity that should be independent of the particular instrument or crystal used is the integral k-ratio for a given accelerating voltage and take-off angle.

This is demonstrated in Table I, where a number of area and peak k-ratios are presented for carbon- $K\alpha$ in near-stoichiometric TiC and ZrC , relative to Fe_3C as a

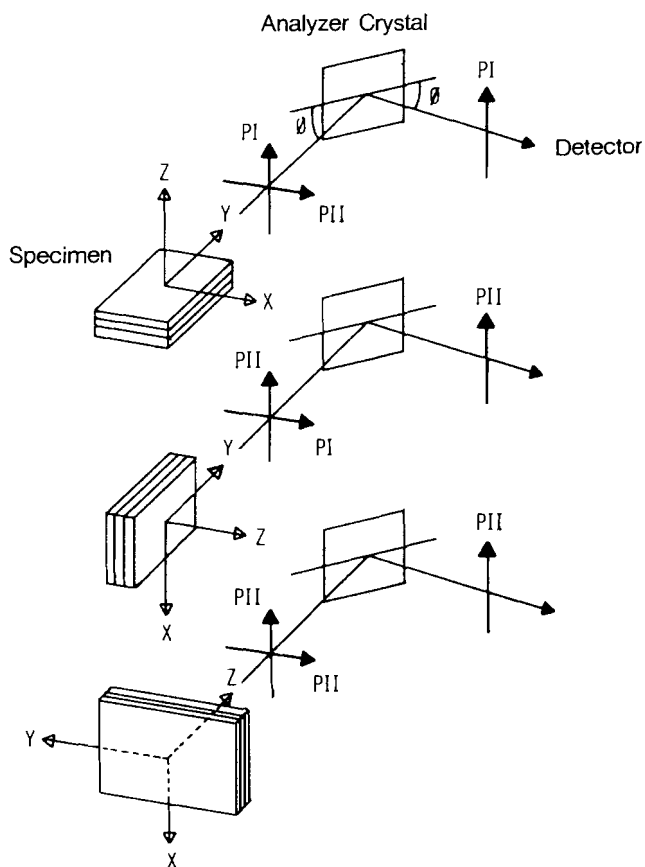


FIG. 6 Schematic drawing showing the interaction of the analyzer crystal with the polarized components in the emitted $B-K\alpha$ radiation. The electron beam is considered to hit the specimen in the origin of the coordinate system X, Y, Z. (After Wiech 1981).

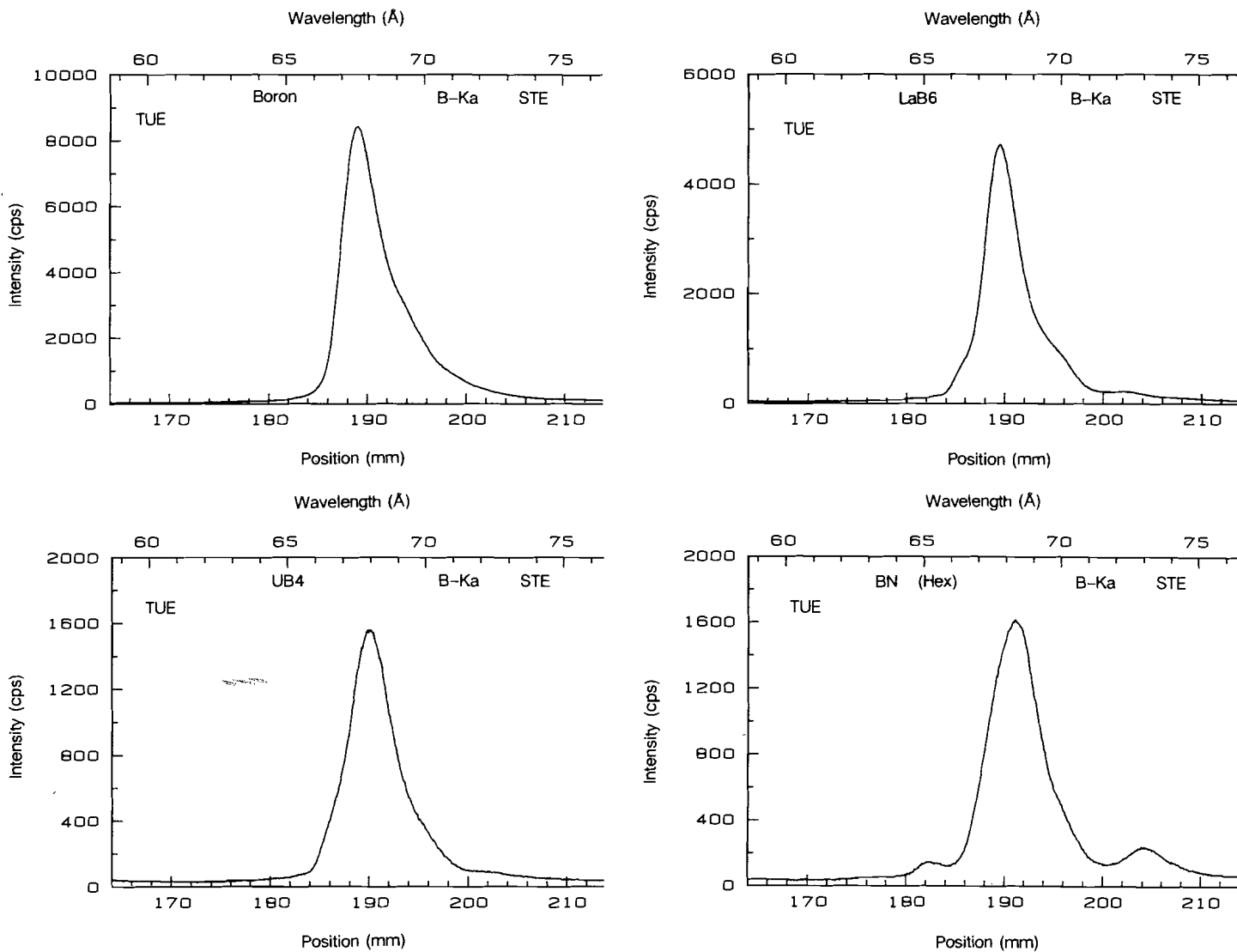


FIG. 7 B-K α peak shapes in B, LaB₆, hex. BN and UB₄. Exp. conditions: 10 keV, 300 nA, stearate crystal.

standard for both the Pb-stearate and the LDE crystal. Table I shows the large deviations, especially for the STE crystal, of the APF from unity. The much lower values for the STE crystal compared with the LDE crystal indicate that the resolution of the former is substantially better. Table I also shows that the integral k-ratios are the same, within experimental uncertainty, thus showing that whereas the peak k-ratios are more or less the accidental results of the use of a particular crystal, the integral k-ratios are really the more fundamental quantities.

Reports from colleagues with comparable instruments (in terms of crystal and resolution) indicate that the same APF values apply within experimental error. This should, however, be checked in each case.

The two carbides in Table I represent the cases with the largest shape alterations, expressed in the lowest APF values, which so far have been found for carbon. It must be realized that Fe₃C has been used as a standard

TABLE I Area k-ratios (AKR), peak k-ratios (PKR), and area-peak factors (APF) for C-K α in near stoichiometric TiC and ZrC at 10 keV for stearate and LDE crystal. Fe₃C standard.

Crystal	TiC			ZrC		
	PKR	AKR	APF	PKR	AKR	APF
STE	5.749	4.279	0.744	1.367	0.961	0.703
LDE	4.958	4.297	0.867	1.123	0.978	0.870

here with a peak width of approximately 70% of that of the carbon peak emitted by glassy carbon. Measurements relative to this elemental form of carbon would result in APF values of 0.7 times those relative to Fe₃C. This illustrates again how large the errors are that can be made when shape alterations are neglected.

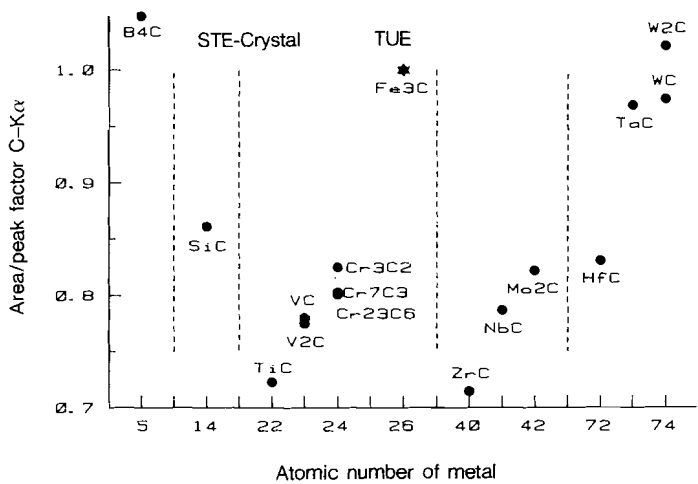


FIG. 8 Area-peak factors for carbon-K α radiation emitted from binary carbides, relative to Fe₃C, as a function of atomic number of the metal partner. The value for Fe₃C is equal to one, by definition (marked by the asterisk). Stearate crystal. Dashed vertical lines mark the transition from one period to another in the periodic system.

When the APFs for C-K α in binary carbides are plotted versus the atomic number of the metal partner, a pronounced saw-tooth-like variation throughout the periodic system becomes visible (Fig. 8). The minimum

values are held by strong carbide formers like Ti, Zr, and Hf while weaker carbide formers like Fe have values much closer to unity.

Using these APF values, a data file of 117 carbon measurements in 13 binary carbides between 4 and 30 keV could be collected and this file has been used for a comparison of the performances of various correction programs, together with various sets of MACs.

For boron the situation becomes much more complex. The 50% of the borides with shape alterations independent of the crystallographic orientation exhibited largely the same pattern as found in the case of carbon, a pronounced sawtooth-like variation with atomic number of the metal partner (Fig. 9). These "fixed" APFs are designated by solid circles. The vertical bars designate the cases with an orientation-dependent APF. The length of the bars indicates the magnitude of the variation of APF observed upon rotation of the specimen. A typical example of this group is ZrB₂, the two extreme peak shapes of which have been shown in Fig. 5. The associated variation in area and peak k-ratio as a function of peak position is represented in Figure 10. Once such variations are known, the intensity measurements can be done on the peak again. After a peak search for each individual grain in the specimen the peak position is used in a graph as in Figure 10, to

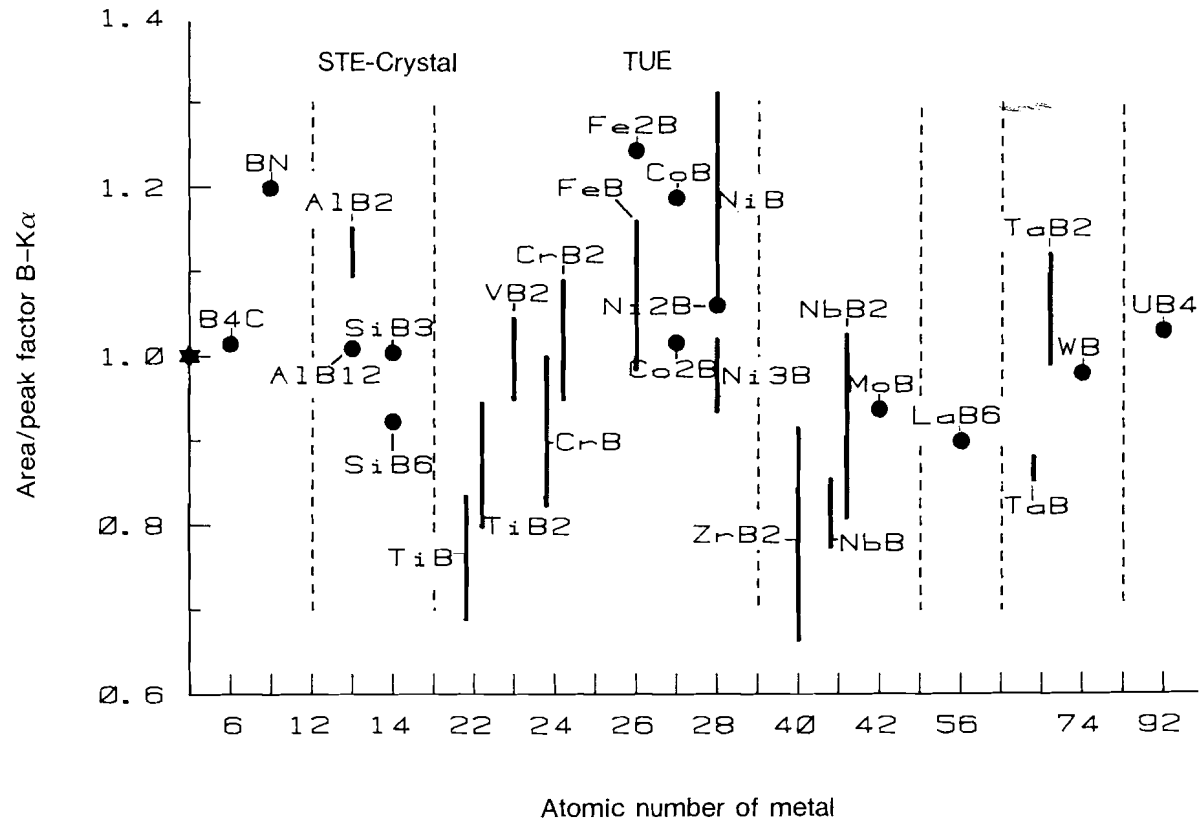


FIG. 9 Area-peak factors, relative to elemental boron (asterisk), as a function of the atomic number of the metal partner for 27 binary borides. Solid circles indicate that no dependence on crystallographic orientation exists. Bars indicate the variation in APF with peak position (crystall. orientation) for the orientation-dependent cases. Stearate crystal. Dashed vertical lines mark the transition from one period to another in the periodic system.

find the appropriate APF and thus the correct area k-ratio. In this way, a total number of 180 boron measurements, relative to elemental boron, in 27 binary borides between 4 and 15 keV (in some cases up to 30 keV) have been collected.

Our experience with nitrogen indicates that the individual APF values, this time relative to Cr_2N as a standard, are much closer to unity than in the previous cases. The maximum deviations are 8%, and in many cases peak shape alterations are only a few percent and can sometimes be neglected altogether. In this case, a data file containing 144 measurements in 17 binary nitrides between 4 and 30 keV has been collected using both STE and LDE crystals simultaneously.

A study of oxygen is near completion at this time. Our experience indicates that peak shape alterations (relative to Fe_2O_3) are almost negligible, at least for the LDE crystal. Maximum deviations are $<2\%$, which is almost within experimental error. The effects for the stearate crystal are probably twice as high. However, problems in the background determination on the short-wavelength side of the oxygen peak, a result of the proximity of the mechanical limit of the spectrometer, prohibit more accurate statements. At the moment, a collection of 344 measurements (on LDE), relative to Fe_2O_3 as a standard, for accelerating voltages between 4 and 40 keV has been realized. For this purpose more than 30 oxides were carefully selected for sufficient electrical conductivity, just as the standard used. Non-conducting oxides, which present a number of specific difficult problems, are the subject of a separate investigation. More details of our work on nitrogen and oxygen will be published in the near future.

What Can be Achieved

Good quantitative results can only be expected from the combination of good measurements and a good matrix correction procedure, in conjunction with the use of a consistent set of MACs.

Tests of matrix correction procedures are usually carried out by comparing the calculated k-ratio (k') for the given composition of a compound to the measured k-ratio (k). The ratio k'/k is usually displayed in a histogram showing the number of analyses versus k'/k . The narrowness of the histogram, expressed in the relative root-mean-square deviation (rms in %) and the final average k'/k value are used as a measure of success for a particular program.

Numerous tests with many correction programs available today in combination with various sets of published MACs for light elements have shown that it is simply impossible for any program to obtain rms values below 10%, and this applies to all the databases for the elements boron through oxygen.

This is very surprising in view of the considerable progress in matrix correction procedures that has been realized in the last decade. It is, therefore, perhaps more likely that the bad results are rather an indication for the average relative accuracy of the published MACs than for the quality of the average correction program. We have collected some evidence to support this assumption.

In our extensive collection of light-element data it is easy to find inexplicable discrepancies between the results obtained for similar compounds of neighbouring elements in the periodic system.

A good example in this respect is the series of carbides ZrC , NbC and Mo_2C . With the MACs for carbon suggested by Ruste (1979) satisfactory results are obtained for NbC while much too low k-ratios are calculated for ZrC and much too high ones for Mo_2C . In the absence of systematic differences in x-ray emission (which is in itself a possibility hardly discussed so far), this must be taken as a strong indication that the MAC for carbon-K α x-rays is much too high in Zr and much too low in Mo. It is very important to realize that such discrepancies between alloys of neighbouring elements can never be explained by improper functioning of any correction program because the latter are invariably based on smooth functions of atomic number Z and atomic weight A , in either an explicit or implicit way.

We feel that it is the particular strength of our databases that they contain many measurements on compounds in which series of consecutive elements in the periodic system are involved, sometimes forming rather complete periods in the periodic system. This makes a consistent evaluation of the results much easier because once it has been established that the combination of program + MACs works satisfactorily for a number of compounds, the results can be extrapolated a few atom-

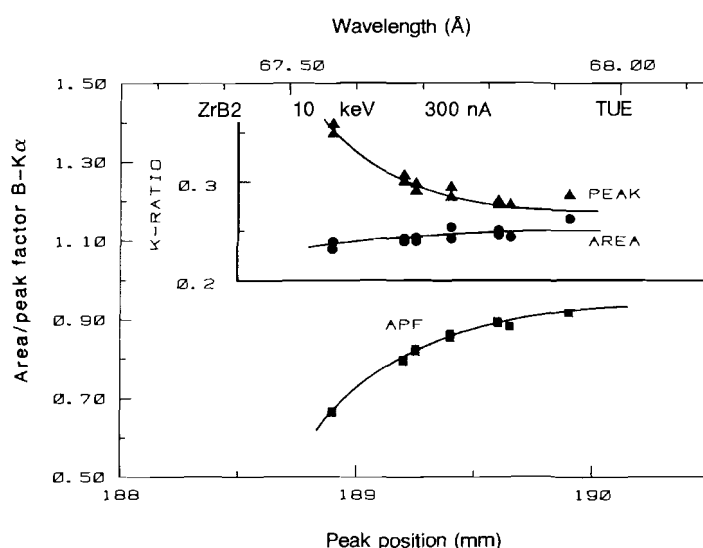


FIG. 10 Variation of peak k-ratio (triangles), area (integral) k-ratio (dots), and area-peak factor (squares) with detected peak position in ZrB_2 (hexagonal structure) as a typical representative of the noncubic borides. Stearate crystal; 10 keV, 300 nA. Reference: Elemental boron.

ic numbers further. If a discrepancy then suddenly turns up (in the absence of absorption edges or other physical restrictions), it is very likely that something is wrong with the MACs rather than with the program. In this light the bad rms figures of 10% and worse are more indicative of the quality of the MACs than of the performance of a correction program. This is all the more so when, as is frequently the case, similar discrepancies are obtained with a number of completely different programs, using the same MACs.

In practice a too low MAC value leads to too high calculated k-ratios and the discrepancies are observed to increase gradually with accelerating voltage. The opposite is, of course, true for too high MAC values. When a series of good measurements is available over a wide range in accelerating voltages it is possible to optimize the k'/k ratio and the rms value at the same time by adjusting the MAC. In the vast majority of cases, the best rms figure is usually obtained in combination with an average k'/k ratio closest to unity. In this way consistent sets of MACs can be produced for each of the light elements B, C, N, and O. Another method to produce consistent MACs is to measure the relative intensity of the light-element radiation emitted as a function of accelerating voltage (Pouchou and Pichoir 1984). The use of a highly consistent program (and an accurate set of measurements) will produce highly consistent mass absorption coefficients.

In some cases we have found evidence that the MAC in a particular element has simply been obtained by (inadvertent) extrapolation of the used equations across an absorption edge. A nice example of this is the case of O-K α in SnO₂. Our measurements for O-K α in RuO₂ between 4 and 40 keV produced excellent agreement with calculations based on Henke *et al.*'s (1974) MAC of 19700 for O-K α in Ru: average k'/k ratio 1.000, rms = 4.32%. The use of the value of 23,100 proposed by Henke *et al.* for O-K α in Sn produced very large deviations for SnO₂ between measurements and calculations: Average k'/k ratio 0.675, rms = 7.011%. The discrepancies were found to increase rapidly with accelerating voltage. A series of tests showed that with a value of 15,050 both an optimum value for the rms was obtained (3.25%) as well as a k'/k ratio closest to unity (0.997). Obviously, the equations used in the calculations of the MAC have been extrapolated across the M5 edge.

In general it was found that the MACs for light element radiations in elements like Zr, Nb, Mo are usually unsatisfactory. The reason for this is quite simple: the vicinity of the M₅ edge in these elements produces a strong and nonlinear variation of MAC with wavelength, which makes inter- and extrapolation very dangerous. In many cases the new values we propose are somewhere intermediate between the older values of Henke and Ebisu (1974) and the more recent ones of

Henke *et al.* (1982); quite frequently, however, the older values seem to be better.

As soon as an absorption edge is passed, the evaluation process has to start anew. Only after a few new cases of satisfactory results is it possible to start making extrapolations. This is yet another reason why so many measurements are necessary on many different systems. In a number of cases it can be necessary even to carry out this process when the composition of the specimen is not known with absolute certainty, which is sometimes the case with carbides and nitrides with wide homogeneity regions. In such circumstances the composition is simply another variable which has to be taken along in the iterative evaluation process. The most likely composition is usually the one giving the best rms value in combination with a k'/k ratio closest to unity. At the same time the MAC value should be consistent with that of neighbouring elements. A great help is the analysis of the x-ray lines of the metal partners over the widest possible range of accelerating voltages. This is the reason why, in addition to the light elements themselves, we usually also measure the metal lines. With a number of uncertain parameters at the same time it is virtually imperative to use all available data that can be gathered. Extensive use is also being made of the latest information on the phase diagrams of the systems in question. The ultimate goal in this process is to achieve the highest possible degree of consistency for all parameters involved.

Finally we will give a brief survey (Table II) of what can be achieved nowadays with a modern correction program (PROZA, for details see Appendix) in combination with consistent sets of MACs. The boron data file contains data for the three Ni-borides Ni₃B, Ni₂B and NiB which exhibit a systematically too low ($\pm 15\%$) emission of B-K α x-rays. The MAC appears to be satisfactory (rms 2–3.7%), but the averages in k'/k vary between 0.84 and 0.87.

TABLE II Results that can be achieved for ultralight element data. For boron and carbon the calculated/nominal concentration (c'/c) has been used in the histogram, whereas for nitrogen and oxygen the calculated/measured k-ratio (k'/k) was used.

Element	Number of measurements	Accel. Voltage (keV)	k'/k (c'/c)	rms (%)
B	180	4–15 (30)	0.977	6–7 ^a
C	117	4–30	0.983	4
N	144	4–30	1.007	4
O ^b	344	4–40	0.998	2.4

^a Significantly better results are obtained when the three nickel-borides, which exhibit approx. 15% too low B-K α emission, are eliminated.

^b Only sufficiently conductive oxides have been included.

General Conclusions

With sufficient care in the measurements and a good correction program in combination with consistent MACs, it is possible to obtain surprisingly good quantitative results for light elements, especially when one takes into consideration that in many cases very extreme conditions have been used, like an accelerating voltage of 40 keV for oxygen. In more moderate conditions, for instance in the range of 8–20 keV, a range which we prefer for a number of reasons, the results would be much better still. At the same time, however, it will be clear that the actual procedures involved in the collection of light element data will always be more time-consuming than those for medium to high Z-elements, due to the pronounced peak shape alteration effects. The future introduction of new multilayer crystals, which have been shown to be less sensitive to these effects, may perhaps produce a further improvement here.

Appendix: Short Layout of PROZA (Phi-RhO-Z and A Correction Program

Introduction

In this new program a drastic change has been made compared with previous versions (Bastin and Heijligers 1986b, Bastin *et al.* 1984c,d, 1986d) in which the $\phi(\rho z)$ parameterizations were based on independent equations for the Gaussian parameters α , β , γ , and $\phi(0)$ in the Packwood-Brown model (1981).

The value of the parameter β is now no longer calculated using an independent equation, but through a procedure based on the atomic number correction of Pouchou and Pichoir (1986). This atomic number correction provides the value of the integral of $\phi(\rho z)$ (i.e., the generated intensity in the specimen) which will be called F. Using the F-value and new expressions for α and γ , the value of β is mathematically adapted in such a way as to ensure that the integral equals F and to ensure at the same time that the peak of the $\phi(\rho z)$ curve has both the "correct" position as well as the "correct" height. This means that the parameters α , β , γ , and $\phi(0)$ are now forced to cooperate in a consistent way in order to provide a specified value for the total generated intensity in the specimen. The main reason why this procedure has been adopted is that now a better and more consistent performance of the correction program must be expected at low overvoltage ratios; an area which has always caused problems in previous versions.

Procedure

Step #1 Calculation of primary (generated) intensity (PI) and integral of $\phi(\rho z)$ ($\equiv F$) according to Pouchou

and Pichoir (1986).

$$PI = R \times 1/S$$

(R = backscattering factor, 1/S = stopping power).

Once the primary intensity is known, the integral of $\phi(\rho z)$ (which is equal to F) can be calculated by dividing the primary intensity by the ionisation cross-section $Q_i(E_0)$ (Pouchou and Pichoir 1986).

$$F = PI/Q_i(E_0)$$

Step #2 Parameterization of Gaussian $\phi(\rho z)$ curves. The object of this step is to find the α , β , γ , and $\phi(0)$ parameters which will provide the correct integral of $\phi(\rho z)$ ($\equiv F$).

(1) The equation for $\phi(0)$ is that used by Pouchou and Pichoir (1986).

(2) Our latest equation for α is:

$$\alpha = \frac{2.1614 \times 10^5 \times Z^{1.163}}{(U_0 - 1)^5 \times E_0^{1.25} \times A} \times \left[\frac{\ln(1.166 E_0/J)}{E_c} \right]^{1.5}$$

in which Z, A, and J are atomic number, atomic weight, and ionization potential of the matrix element. E_0 , E_c , and U_0 are accelerating voltage, critical excitation voltage and overvoltage for the x-ray line in question. For a compound target a matrix of $\alpha_{i,j}$ values (α for element i-radiation in interaction with element j of the matrix) is calculated and the α_i -value in the compound target is composed as follows:

$$(1/\alpha_i)_{\text{comp.}} = \sum_j C_j \times \frac{Z_j}{A_j} \times 1/\alpha_{i,j} / \sum_j C_j \times \frac{Z_j}{A_j}$$

(3) The equation for γ is:

for $U_0 \leq 6$:

$$\gamma = 3.98352 \cdot U_0^{-0.0516861} \cdot (1.276233 - U_0^{-1.25558Z-0.1424549})$$

for $U_0 > 6$:

$$\gamma = 2.814333 \cdot U_0^{0.262702.Z-0.1614454}$$

In order to accommodate the change in ionisation cross-section with atomic number for ultralight element radiations, proposed by Pouchou and Pichoir, it is necessary in these cases to multiply γ further by the equation:

$$E_c \div (-4.1878 \cdot 10^{-2} + 1.05975 \times E_c)$$

This is only necessary if $E_c < 0.7$ keV. For a compound target the weight-fraction averaged atomic number is substituted for Z.

(4) The calculation of β proceeds in the following way: We have shown before (Bastin and Heijligers 1984c) that the total intensity generated in a specimen ($\equiv F$) can be expressed by:

$$F = \frac{[\gamma - (\gamma - \phi(0)) \times R(\beta/2\alpha)] \times \sqrt{\pi}}{2\alpha}$$

in which $R(\beta/2\alpha)$ is the fifth-degree polynomial used in the approximation of the $\text{erfc}(\beta/2\alpha)$ function. In fact, the latter equation is the formal solution of the Gaussian integral of $\phi(\rho z)$ between 0 and infinity in closed form. After rearranging it follows that:

$$R(\beta/2\alpha) = [\gamma - 2\alpha \times F/\sqrt{\pi}]/[\gamma - \phi(0)]$$

Contrary to our previous versions this time F is known first and the problem is now to find the value of β using the known values of α , γ , and $\phi(0)$ through the latter equation. This means that the function $R(\beta/2\alpha)$ has to be used backward: i.e., the function value is known and the argument ($\beta/2\alpha$) has to be determined.

The simplest way to solve this problem was to cut the function into 9 different regions and to fit these regions with much smaller geometric functions. If for a moment we substitute x for $R(\beta/2\alpha)$, we obtained as the best fits:

$.9 \leq x < 1$	$\beta/2\alpha = .9628832 - .9642440.x$
$.8 < x < .9$	$\beta/2\alpha = 1.122405 - 1.141942.x$
$.7 < x \leq .8$	$\beta/2\alpha = 13.43810.\exp(-5.180503.x)$
$.57 < x \leq .7$	$\beta/2\alpha = 5.909606.\exp(-4.015891.x)$
$.306 < x \leq .57$	$\beta/2\alpha = 4.852357.\exp(-3.680818.x)$
$.102 < x \leq .306$	$\beta/2\alpha = (1 - .5379956.x)/(1.685638.x)$
$.056 < x \leq .102$	$\beta/2\alpha = (1 - 1.043744.x)/(1.604820.x)$
$.03165 < x \leq .056$	$\beta/2\alpha = (1 - 2.749786.x)/(1.447465.x)$
$0 < x \leq .03165$	$\beta/2\alpha = (1 - 4.894396.x)/(1.341313.x)$

As a result of the fitting procedure, the value of $R(\beta/2\alpha)$ thus obtained will never be exactly the same as the one calculated before, especially near the transition points of one function to another. In an extra loop in the program the approximated value of $R(\beta/2\alpha)$ is compared to the formal one and β is adjusted in an iterative procedure in order to produce a specified relative precision (at the moment 0.1%) in the approximated value of $R(\beta/2\alpha)$ as compared to the formal one.

Once α , β , γ and $\phi(0)$ are known the usual procedure (Bastin *et al.* 1984d) can again be followed. A special precaution had to be taken at extremely low overvoltages. In such cases it is virtually impossible to ensure a correct parameterization of $\phi(\rho z)$ curves due to the extreme delicacy involved in the balance of

parameters which are still expected to produce the specified F -value. Thus it can happen occasionally that $R(\beta/2\alpha)$ values are calculated which are negative or larger than one. It is obvious though, that $R(\beta/2\alpha)$ can only have values between 0 and 1, which means that β is between infinity and zero. When $R(\beta/2\alpha)$ is outside these limits then the normal parameterization route cannot be used and an auxiliary procedure has to be followed. In these (rare) cases the calculated value of α is dropped and for a start it is assumed that the $\phi(\rho z)$ curve starts halfway the value of $\phi(0)$ and γ . Using the known value for F a new (and usually higher) value for α is calculated through:

$$\alpha = \frac{[\phi(0) + \gamma] \times \sqrt{\pi}}{4 F}$$

The value of $R(\beta/2\alpha)$ is thereby set at exactly 0.5. Although the $\phi(\rho z)$ curves in such cases may not be 100% realistic, the answers returned by the program are still very good because the atomic number correction is still consistent and the effects of (slight) shifts in the peak of the $\phi(\rho z)$ curves have a negligible influence on the magnitude of the absorption correction under these circumstances. The advantage of the new program is that it can now be used down to the lowest possible overvoltages (if one insists on working under these difficult conditions). Its performance on a data file of 877 measurements [Bastin *et al.* 1986d, file

supplemented with metals analyses in borides (Bastin and Heijligers 1986b)] of medium-to-high Z elements is:

$$\text{Average } k'/k \text{ ratio: } 0.9955 \\ \text{rms: } 2.44\%$$

The results for light elements are represented in Table II.

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*It should be noted that there is an error on page 251 of this reference: In the equation for the primary intensity I the ratio

$$\left(\frac{U_0}{V_0}\right)^{PK}$$

behind the Σ -term should read:

$$\left(\frac{V_0}{U_0}\right)^{PK}$$