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MATERIALS CHARACTERIZATION USING THE BACKSCATTERED
ELECTRON SIGNAL IN SCANNING ELECTRON MICROSCOPY

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Abstract

The backscattered electron signal in scanning electron microscopy is sensitive to changes in the atomic number of the specimen. This atomic number information can be measured by calibrating the output of a backscattered electron detector from two known materials. The atomic number of an unknown sample can then be determined by measuring the backscattered electron signal from the unknown sample.

Knowing the atomic number factor of an unknown sample and the heavy elements ($Z > 10$ as determined from X-ray analysis), the existence of light elements can be detected. From a knowledge of the sample and valence information, the composition of a sample can often be characterised in terms of its chemical formula.

KEY WORDS: Backscattered electron detector, atomic number factor, valence, chemical formula.

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Introduction

Since their widespread availability in the 1960's, scanning electron microscopes (SEMs) have shown themselves to be very powerful tools for the in situ microanalysis of particles and specimens. Initially, the major electron detector used was the Everhart and Thornley (1960) detector. This was primarily a secondary electron detector and was used almost exclusively for imaging. Microanalysis for elemental composition became a possibility with the introduction of X-ray detectors, namely energy dispersive (Fitzgerald et al., 1968; Ogilvie, 1969; Russ & Kabaya, 1969) and wave length dispersive detectors (Castaing, 1951; 1960; Castaing and Guinier, 1950; Castaing and Descamps, 1955). As well as recognising elements from the wave length of the X-rays, techniques were developed which enabled these detectors to determine the proportions of the various elements present (see for example, Poole and Thomas, 1962; Philibert, 1963; Martin & Poole, 1971; Reed, 1975; Ruste & Zeller, 1977; Parobek & Brown, 1978; Love & Scott, 1978; 1981).

Other techniques incorporated in SEMs include Auger electron spectrometry (MacDonald, 1970; 1971) cathodoluminescence (Muir & Holt, 1974; Holt and Saba, 1985; Trigg, 1985), scanning acoustic microscopy (Vetters et al., 1985). All of these techniques represent different ways of characterizing a sample being studied.

In its broadest context, the word "characterize" means to note any distinguishing features (about a sample). Backscattered electron detectors (BSEDs) provide a different way of looking at specimens in the scanning electron microscope. They can provide information which is different from that obtained by the abovementioned techniques and, as such, provide another way of characterizing materials.

This paper describes some of the ways that BSEDs can be used to obtain information about the sample. The differ-

ent types of backscattered electron detectors available have been reviewed (see for example, Robinson, 1979). The electron backscattering process which gives rise to the signal detected by these detectors has been reviewed (see for example Niedrig, 1978).

Background

The major features of the back-scattered electron (BSE) signal are its strong variation with atomic number of the specimen and its high signal to noise. The first technique using backscattered electron detectors to characterize specimens, involved using these detectors to notice differences in atomic number. Higher atomic number materials would show out at a greater intensity, as shown in Figure 1. Often a knowledge of the sample plus the intensity and shape of a particle as seen in the BSED image, was sufficient to enable complete determination of that particular particle. For example, the rectangular shape of the bright phase in Figure 1, is sufficient to establish it as galena (PbS). Pye and Krinsley (1983) have illustrated how this can be used to separate several minerals.

However, the most common method of using BSEDs for materials characterization, is to use them to locate phases of different intensity, then use X-ray analysis techniques, particularly energy dispersive X-ray spectrometry (EDS), to determine the elements present in the material and their relative proportions. The advantages of using the BSE signal over the secondary electron (SE) signal

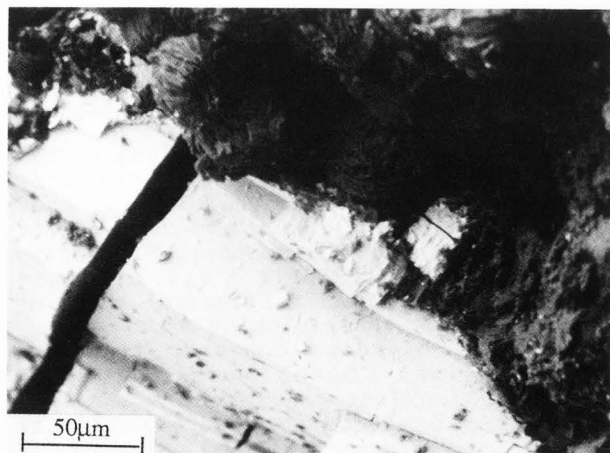


Figure 1. Micrograph of galena (PbS) in a fracture surface with an aluminosilicate matrix. The relative brightness and the rectangular fractures combined with the knowledge that this sample came from a lead bearing ore, establish that the particle was galena. 25kV, 0 deg. tilt, wide angle BSE detector.

are clearly seen in Figure 2. Figure 2a shows the image of a lead zinc ore, obtained using a BSE detector, Figure 2b shows the image of the same region, obtained using an Everhart Thornley (E-T) detector. The BSE image shows the phases with much greater accuracy and integrity than can be seen with the SE image. Whilst this technique does not give complete characterization of the particular phases, it does make it considerably easier to use the EDS to determine the elements present and from that determine the composition of individual phases. This combination of BSE and EDS analysis, is widely used in many aspects of materials characterisation (Robinson & Robinson, 1978; Robinson & Nickel, 1979; Hall & Lloyd, 1981).

A technique related to this is the use of heavy metal stains in biological tissues and locating these stains with a

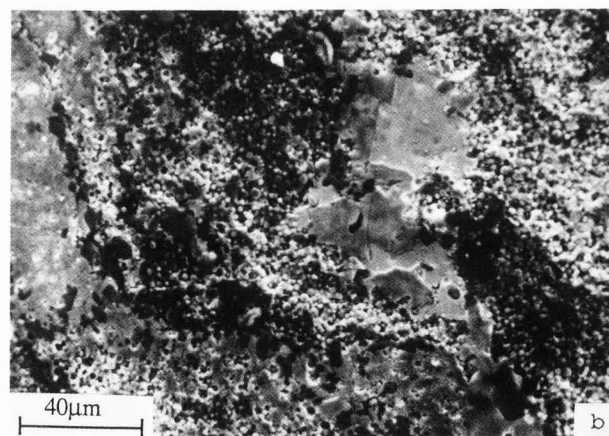
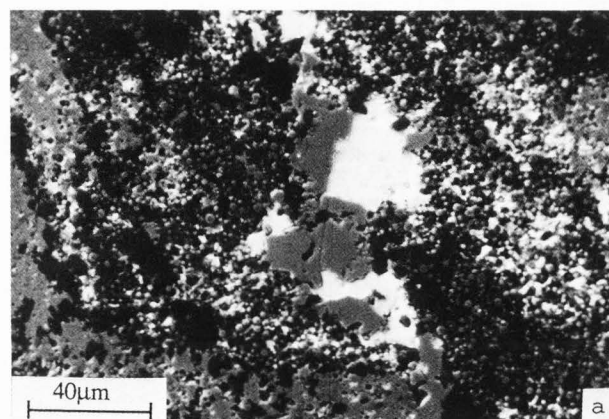


Figure 2. Wide angle BSE image (a) and SE image (b) of a lead zinc ore. The phases, as seen in the BSE image are, in order of decreasing intensity: galena (PbS), sphalerite (ZnS), pyrite (FeS₂), quartz (SiO₂). 25kV, 0 deg. tilt. These phases are more easily recognised in the BSE image (a) than the SE image (b).

BSED (Becker and Sogard, 1979; Hoyer et al., 1979; Walther et al., 1984). Metal stains used include silver and gold. The uptake of the heavy metals plus their position characterizes the types of cells and specific positions of certain features, e.g. antibodies. The uptake of heavy metal contaminants by cells for example, from contaminated water, can also be detected and used to characterize the sample (Jablonski and Lytton, 1980).

The important features of the above described applications were that the separate intensities were used to distinguish different materials. However, at no stage was there any attempt to either process or measure BSE signals or intensities. One of the first detection systems to process the BSE signal, was the solid state pair detector system of Kimoto & Hashimoto (1966). By adding the signals from two equispaced detectors, the atomic number contrast could be enhanced and the topographic contrasts suppressed. Subtracting the two signals enhanced the topography contrast whilst suppressing atomic number contrast.

The use of this addition or subtraction process has shown itself to be useful in separating contrast effects due to topography and atomic number. A variation of this was a small, solid angle scintillator detector with an adjustable takeoff angle (Schur et al., 1974). By changing the position of this detector it was possible to alter contrast effects due to crystalline structure. Neither of these techniques has found widespread usage in the SEM characterization of materials.

Ogilvie (1969) and Colby (1969) were amongst the first to try to determine composition of materials by measuring the intensity of the backscattered electron signal. In both cases they were attempting to measure the backscattered electron yield from a binary alloy to determine the relative amounts of the two components present in it. They achieved limited success. More recently Ball and McCartney (1981), Hall and Lloyd (1981) and Marquis (1981) have attempted more sophisticated measurements of the BSE signal in an attempt to determine atomic number and composition of materials in the SEM. Again they were only partially successful. They used the BSE yield in their calculations but measured the output from a BSE detector. This approach gave reasonable agreement when high atomic number materials were mixed in alloys, but failed to give an adequate match when low atomic number materials were included.

Composition Analysis

Robinson et al. (1984) overcame this limitation. They found that the signal output from a BSED always varied in a

fixed manner, with a variation of atomic number. This variation is shown in Figure 3, as a curve of BSE detector signal output against atomic number for a series of known elements. The shape of this curve varies with the surface work function of the detector. Apart from that, it is uniform for acceleration voltages above 15 kV and is independent of the beam current, working distance or specimen tilt providing it is less than ± 10 degrees. Fixing any two points on that curve, fixes the signal variation with atomic number. Provided all other contrast effects have been removed - e.g., topography, charging, crystalline orientation - a variation of detector signal output can only be due to a change of atomic number and it will follow this curve exactly. This means that, if you fix any two points on that curve, i.e., measure the BSED signal output at two known atomic numbers, it is easy to use this curve to predict the signal output from any other material of known atomic number. Alternatively, by measuring the signal from a BSED, you can determine the atomic number of the material being examined.

This technique thus offers the possibility of using the BSE signal to determine an element by measuring its atomic number. However, EDS and WDX are two well established techniques that can determine prime elements better than this technique, making it of little benefit if this were the only feature. Fortunately, by using a modification of the Castaing (1960) relationship governing the backscattered electron yield or output from a composite sample - one containing two or more elements - the BSE yield for a composite sample can be calculated (Robinson et al., 1984) via the relationship:

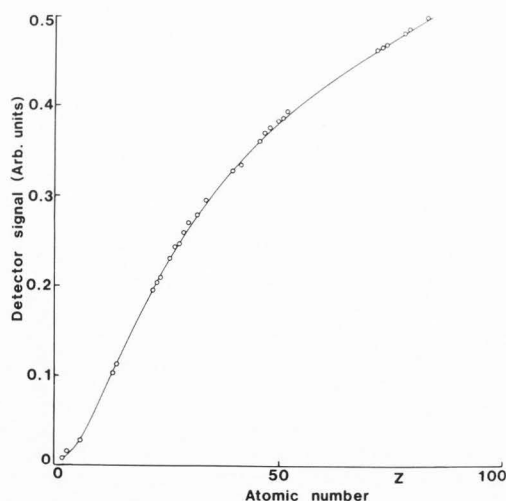


Figure 3. Curve of BSE detector signal output versus atomic number.

$$S_{\text{comp}} = \sum_{i=1}^n S_i X_i \quad (1)$$

S_{comp} is the expected signal from the composite sample, S_i and X_i are the BSE signal and weight fraction of the i^{th} component of the compound. The weight fraction is given by:

$$X_i = \frac{A_i}{\sum_{j=1}^n A_j} \quad (2)$$

where A_i and A_j are the atomic weights of the i^{th} and j^{th} elements respectively. This relationship is based upon the Castaing (1960) relationship, which was also verified by Herrmann and Reimer (1984).

By extrapolating the calculated S_{comp} back to atomic number via the curve shown in Figure 3, an atomic number factor (ANF) can be calculated for any compound or combination of any number of elements.

The atomic number factor of a compound determined by this technique has a number of important properties:

1). The atomic number factor of an element is the atomic number of the element. 2). The atomic number factor of a compound, alloy or mixture of elements can be calculated from a knowledge of the elements present and the ratios in which they are mixed - i.e., the chemical formula. 3). The atomic factor of a compound can be matched to the BSE signal from a sample of the same composition.

The atomic number factor of a compound, should be thought of as the atomic number of the components of the compound, averaged according to weight percent, electron scattering cross-section and detector response. This averaging is used instead of averaging according to atomic weight, because this is the only method available in which theory and experiment can be matched.

To determine the atomic number factor of a compound first calculate its molecular weight. This is done by adding up the sum of the atomic weights of all the components in the compound. Then take each element in turn and determine its weight fraction. The expected signal from each element is then determined by starting at the atomic weight of the element, moving up to the signal curve and calculating the signal expected from a pure element. The signal contribution from that element is determined by multiplying this pure element signal by the weight percent of the pure element in

the compound. This procedure is repeated for all the elements in the compound.

As mentioned earlier, this technique is based upon the Castaing (1960) relationship. It is equivalent to saying that the atoms of each element scatter electrons as if they were independent of other atoms: the atoms of each element screen the electrons from other element atoms, i.e. they reduce the probability of an electron being scattered by other atom electrons: the atoms of each element are, in turn, screened by the atoms of the other electrons. An example is given hereunder, in the calculation of the atomic number factor for calcium carbonate (CaCO_3).

Calcium has an atomic number of 20 and atomic weight of 40. Carbon has an atomic number of 6 and an atomic weight of 12. Oxygen has an atomic number of 8 and an atomic weight of 16. CaCO_3 is composed of one Ca atom, one C atom and three O atoms, giving it a molecular weight of $40 + 12 + (3 \times 16) = 100$. The Ca contribution to the CaCO_3 signal is worked out by going along the atomic number axis to 20, see Figure 4, then going vertically upwards to the signal curve and then horizontally across to the signal axis to determine the backscattered electron signal expected from pure Ca. However, Ca constitutes only 40 percent of the weight of CaCO_3 and therefore the Ca contribution to the CaCO_3 signal will be 40 percent of the pure Ca signal.

Next, consider C, atomic number 6 and again determine, from the signal curve, the signal expected from pure C. C represents only 12 percent of the weight of CaCO_3 and therefore the C contribution in CaCO_3 will be only 12 percent of the signal from pure C.

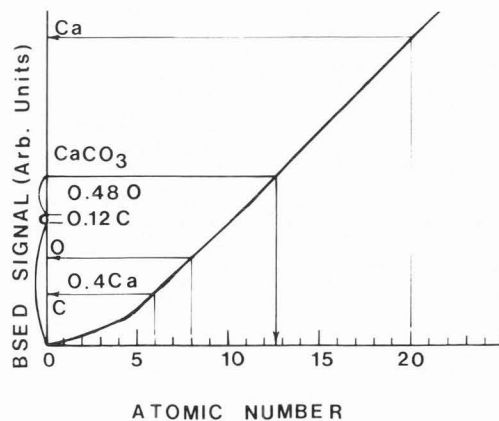


Figure 4. Illustration of the technique used in composition analysis to determine the atomic number factor of a compound (CaCO_3).

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Moving onto O, atomic number 8, determine, from the signal curve, the expected signal from pure O. O constitutes 48 percent of the weight of CaCO₃ and the expected O signal is thus 48 percent of the signal from pure O. Add this signal to the previous signals from Ca and C and get the total expected backscattered electron signal from CaCO₃. Having obtained the signal from CaCO₃, go in the reverse direction, back to the curve and then down to the atomic number axis and the atomic number so given is the atomic number factor for calcium carbonate, namely 12.8. This is illustrated in Figure 4.

By this technique, each element makes a contribution to the final signal output from the BSE detector. Equally important, the effect of each element can be calculated. This has two advantages: i). Where all elements in a sample are known, it is possible to check the accuracy of the technique. This was done previously and some of the results are shown in Table 1 (Robinson et al., 1984). ii). When elements are unknown there exists the possibility of determining these unknown elements and the amounts present.

Determining the Atomic Number Factor

The output of a BSE detector depends upon a number of factors. These include: i). SEM accelerating voltage E_B , ii). Beam current I_B , iii). Detector efficiency, iv). Atomic number of the specimen, v). Detector collection angle, and vi). Gain of the detector.

This can be summarised by the equation:

$$S_{det} = E_B I_B \eta \Omega C_e F(\Omega) F(Z) G \quad (3)$$

where η is the BSE yield, Ω is the solid angle of collection, C_e is a term taking into account the conversion efficiency of the detector, $F(\Omega)$ and $F(Z)$ are functional terms relating to variation of BSE detector output with collection angle and atomic number respectively and G is detector gain.

Varying any one of these will alter the output of a BSE detector. Consequently, before you can make use of this atomic number information, it is necessary to align the detector output signal with the atomic number information in the specimen. This is done simply by measuring the voltage output from the detector at two known atomic numbers. These can be either a Faraday cage and one known sample, or two known samples. Once two points on the BSE detector signal versus atomic number curve have been

fixed, any variation in output from the BSE detector can only be due to a variation in the atomic number of the specimen. Further, the change will follow exactly the curve shown in Figure 3. The output of the BSE detector can be converted directly from a voltage reading into atomic number factor.

Table 1 Calculated and measured atomic number factors for a range of compounds. In the purity determination, "Analytical" indicates the sample studied was a purchased laboratory grade chemical of known purity, "WDX" indicates the formula was confirmed by wavelength dispersive X-ray analysis; "Commercial" indicates the sample was nominally of the indicated formula, but no positive confirmation was available. (Robinson et al., 1984)

Compound Formula	Calculated ANF	Measured ANF	Purity Deter- mination
LiF	7.6	7.9	Analytical
NaCl	14.7	14.6	Analytical
SiO ₂	10.9	10.8	WDX
FeS ₂	20.4	20.4	WDX
MoS ₂	29.2	29.2	Commercial
PbS	66.3	66-67	Commercial
PbSO ₄	46.0	45.8	Analytical
KCl	18.0	18.0	Analytical
FeO	21.7	21.5	WDX
Fe ₂ O ₃	20.3	20.3	WDX
CuFeS ₂	23.2	23.1	Commercial
ZnS	24.8	25.0	Commercial
Al ₂ O ₃	10.7	10.6	WDX
Al ₂ O ₃ ·2H ₂ O	9.9	9.8	Commercial
GaP	25.4	25.2	WDX
MgO	10.5	10.6	WDX

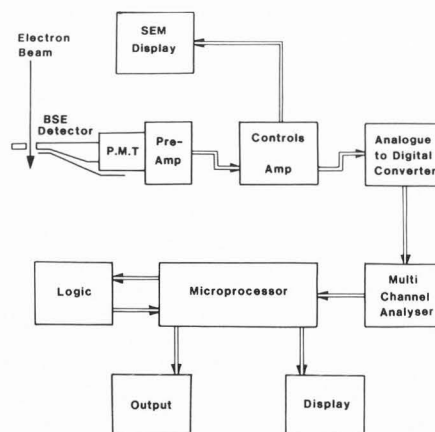


Figure 5. Schematic illustration of the incorporation of a microprocessor into a system capable of performing composition analysis measurements.

To take advantage of this information, composition analysis systems have been constructed. These have been based upon a microprocessor and are schematically illustrated in Figure 5. The system consists essentially of a BSE detector and amplifiers, an analogue to digital converter (ADC), microprocessor, multi-channel analyser (MCA) and software.

The signal from the detector is amplified, fed into the ADC and displayed on the MCA display. The horizontal axis of the MCA, displays the amplified output of the BSE detector, typically 0 to +10V. However, by stating that two particular voltages correspond to specific atomic numbers, the horizontal axis can be displayed directly in terms of atomic number factor. Then, provided there is no change in the microscope operating parameters, beam voltage and current, working distance and specimen tilt, the output from the detector is registered directly on the MCA as an atomic number factor.

Analytical Capabilities

The primary data obtained from composition analysis is the atomic number factor of the phase or specimen. However, this is not a unique number because there are many materials that can have the same atomic number, e.g., SiO_2 at 10.9, and Al_2O_3 at 10.7 are indistinguishable because of experimental error. However, they can be easily distinguished by other techniques, e.g., energy dispersive X-ray spectroscopy (EDS) or wavelength dispersive X-ray spectroscopy (WDX), to distinguish between the Si and Al.

Combining the data from EDS and composition analysis gives the primary data of the elements present, including the amounts or relative proportions of these elements, and the atomic number factor of the sample. To completely characterize the sample, the task becomes one of combining these two pieces of information to determine its composition (formula).

To assist in this task, a number of simple concepts can be applied: i). If the heavy elements and their ratios, as detected by X-ray analysis, have the same atomic number factor as that measured from the sample, there are no light elements present. ii). There is only a limited number of light elements. iii). Light elements most frequently combine with heavy elements in a limited range of associations. This can be either through valence bonding to form a compound or through alloying to form a composite material. Only in rare or unusual circumstances will light elements form a mixture of infinitely variable composition. (A light element is defined as

having an atomic number between 1 and 10 inclusive. They are not easily detectable in a Be window EDS analysis.)

It is possible to use this information, the atomic number factor, the heavy elements from EDS, the limited number of light elements and the valence of the elements to determine the chemical formula of the specimens being studied.

In chemical bonding to form compounds, elements gain or lose electrons to form a bond with the atoms of another element. Once an atom has gained or lost an electron through this type of action it is called an ion. There are only two types of ions:

Cations - those which lost one or more electrons to become positively charged.
Anions - atoms which gain one or more electrons to become negatively charged.

Whenever two or more elements combine to form a compound, they do so in a manner that ensures the total charge on the compound is nil. In any compound, the total sum of the positive charges from all cations equals the total sum of the negative charges from all anions.

This principle can be applied to the measurements from composition analysis and EDS. There is only a limited number of light elements and light element combinations. A list of the most commonly encountered light element anions is shown in Table 2. Whenever a single metallic (cation) element is detected by EDS, it can be combined, in valence proportions, with all of the list of light anions and the atomic number factor of the resulting compound calculated. If the match between the calculated and observed atomic number factors is not good, it means that the sample being analysed is not the compound formula just calculated. If there is a match between the calculated and observed ANFs, it indicates that the sample being studied may be the compound whose formula has just been calculated.

Sometimes there can be a match of two or more compounds of the same heavy element and different light elements, producing the same atomic number factor. For example, CaCO_3 and $\text{Ca}(\text{CN})_2$ have, within experimental error, the same atomic number factor, 12.8. Composition analysis and EDS cannot distinguish between these two compounds. However, it can eliminate all other compounds and the application of some limited knowledge of the origins of the sample would help to make the choice between the two.

A similar procedure can be used for two heavy elements. Possible combinations of the heavy elements with light elements can be considered for both compounds and mixtures of compounds and a determination made of the relative amounts of the heavy elements present. If this ratio agrees with the heavy element ratio as determined

Table 2. List of commonly used anions.

Formula	ANF	Valence
H	1.0	-1
N	7.0	-3
O	8.0	-2
F	9.0	-1
BeO ₂	7.2	-2
BO	6.7	-3
BO ₂	7.2	-3
BO ₃	7.4	-3
CN	6.5	-1
HCO ₂	7.3	-1
C ₂ O ₄	7.4	-2
B(C ₆ H ₅) ₄	5.8	-1
H ₄ C ₄ O ₆	7.2	-2
H ₃ C ₂ O ₂	6.9	-1
HCO ₃	7.5	-1
CO ₃	7.6	-2
OH	7.7	-1
NO ₂	7.7	-1
NO ₃	7.8	-1
O(OH)	7.8	-3
O ₂	8.0	-2
BF ₄	8.5	-1

by EDS, it is an indication that the sample being studied may have the composition of the formula calculated. If there is no match of the heavy element ratio, the sample does not have the composition of the formula calculated.

When three or more elements are detected by EDS, such an analysis can only be performed for a specific light element, e.g., oxygen, to see if a match can be obtained for valence and heavy element ratios. There is considerable scope left for improving the analytical capability of this aspect of composition analysis.

Applications

i). Locate boron in an aluminium alloy containing nominally 5% by weight titanium, 1% by weight boron, the remainder being aluminium.

Conventional EDS offered no practical solution. The BSE detector image shows two separate phases (see Figure 6). EDS analysis of the grey matrix reveals aluminium. Composition analysis, Figure 7, indicates this phase has an ANF of 13.0. These two pieces of information combine to determine that this phase contains only aluminium. EDS analysis of the brighter phase shows that it contains the heavy elements aluminium and titanium. Quantitative analysis shows

that these elements are combined in the atomic ratios of 1.5 Al to 1.0 Ti. If the material in this phase was Al_{1.5}Ti, it would have an ANF of 17.7. Composition analysis of this phase yields an ANF of 16.4. The fact that the ANF is 16.4, i.e. lower than 17.7, indicates the presence of light elements. Analysing for boron, reveals that the phase has the composition Al_{1.5}TiB. EDS and composition analysis have combined to show that the boron was in the bright phase along with aluminium and titanium and was not distributed throughout the aluminium matrix.

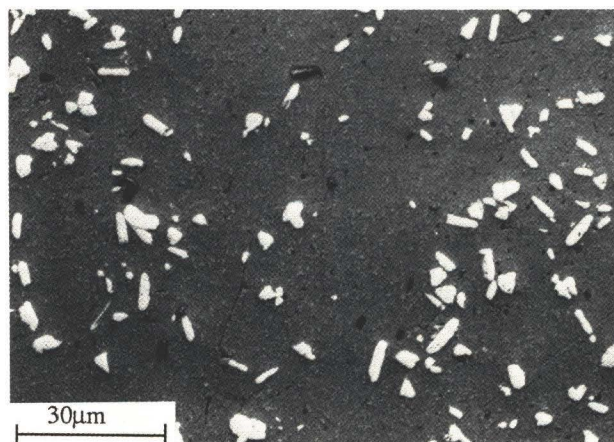


Figure 6. BSE image of an Al, Ti, B alloy showing two separate phases. 25kV, 0 deg. tilt.

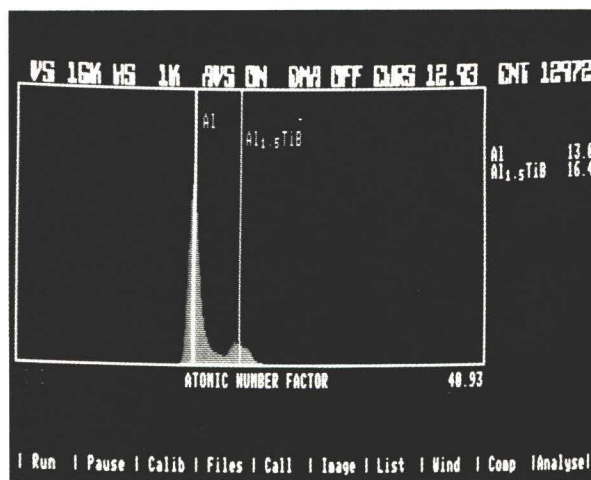


Figure 7. Composition analysis spectrum of the Al, Ti, B alloy shown in Figure 6. The peak corresponds to the individual phases and have ANFs of 13.0 and 16.4 respectively.

ii). Determine how much beryllium was present in a particular copper/beryllium alloy.

The BSE detector image showed a single phase material. EDS analysis yielded only copper. Composition analysis yielded an ANF of 28.4. The measured ANF of 28.4 is obviously lower than pure copper indicating the presence of a light element. Ratioing Cu and Be to obtain an ANF of 28.4 yielded that the material had a composition of $\text{CuBe}_{0.15}$. This corresponds to approx. 2% by weight of beryllium in the copper.

iii) Corrosion and contamination can represent major problems for industry. The corrosion and contamination products are often simple compounds containing light elements - is it an oxide, carbonate, nitrate or hydroxide? Analysis by conventional EDS reveals very little, while WDX analysis can be expensive and slow. The following examples illustrate how EDS can combine with composition analysis to solve these problems.

a. Identify the contaminant spots on a mild steel housing. EDS analysis shows iron (Fe) as the only detectable heavy element. Composition analysis shows these spots as having an ANF of 20.4. Checking the ANFs of all Fe compounds formed from light elements yielded the formula Fe_2O_3 as the only possibility, showing the contamination to be rust spots and not a more complex structure.

b. Copper tubing was corroding away, leaving a solid residue. EDS analysis shows copper (Cu) as the only detectable heavy metal. Composition analysis yields an ANF of 24. Again checking the ANFs of all Cu compounds formed from light elements, generated the list of possible formula.

CuOH

CuF

CuO

$\text{Cu}_3(\text{BO})_2$

CuF and $\text{Cu}_3(\text{BO})_2$ were eliminated because of the lack of a suitable source of the anions. CuOH is not a stable compound. This left CuO as the only suitable compound indicating that the corrosion product was a simple oxide.

Conclusions

The signal output from a BSE detector can be used in conjunction with the information obtained from EDS, to help determine the chemical composition or formula of a specimen being studied in a SEM.

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Discussion with Reviewers

R.P. Becker: Have you applied this method to biological or other low Z samples, whether dry, frozen hydrated, or wet in an environmental chamber? If not, how useful would you expect this method to be on such samples?

Author: No. The sensitivity of the technique is not sufficient to enable it to distinguish, with any reasonable degree of certainty, between all of the different types of organic materials. They have an atomic factor range from approximately 5.5 for hydrocarbons - $(CH_2)_n$, to 6.8 for carbohydrates - $(C_6H_{12}O_6)_n$, with water only extending this range up to 7.2. As it is currently operating, this technique has an error of approximately 0.2. This is not sufficient for it to be able to reliably used to identify many organic/biological materials. However, it could be useful for making some distinction between some different types of organic substances. Obviously there is room for further research in this regard.

R.P. Becker: Can this method be used at low kV (e.g. 1 kV) with a suitable detector?

Author: Yes. Such a system would enable the same type of analysis to be carried out in the SEM on surface structures which are only tens of nanometers thick.

H. Niedrig: Can you refer on the limits of the measuring accuracy in cases where
i) the range of crystalline particles becomes smaller than the electron range?
ii) the lateral dimension of the specimen becomes smaller than the electron range?
In these cases, the backscattered signal will differ from that of a bulk target of this material.

Author: When the signal originates from a volume less than the electron penetration volume, this technique cannot be used. It is possible to calculate the effects of reduced particle size, but these calculations have not yet been done. One practical way of performing an analysis on small particles is to carry out this type of analysis at several different accelerating voltages and extrapolate the results to a low voltage.

V. Thien: Why is a signal prediction of known atomic number Z necessary?

Author: I have shown the ability to predict the atomic number of known materials, in order to show that the technique works.

H. Niedrig: You speak of the "surface work function of the detector." What do you mean by this term?

Author: The surface work function of the detector is the average energy lost when an electron enters the detector. An electron of very low energy does not have sufficient energy to give off a signal when it impinges upon the detector surface, This is due to the dead layer on the surface of any material. This dead layer can be made up from contamination layers, or damage to the surface of the detector.

H. Niedrig: The shape of the detector signal versus atomic number curve also depends on the solid angle, see, e.g., F.J. Hohn: Angular dependence of electron intensities backscattered by carbon films, Optik 47 (1977) 491-494. Therefore, a full calibration curve for every detector arrangement without 2π geometry will be necessary. Do you agree?

Author: No. The angular dependence shown was for a small solid angle at each measurement. The detector we provide measures over a large solid angle. As such, it averages all of those variations. Remember also, the detector has a large solid angle that has a fixed average takeoff angle. We specify that the results are only valid if the specimen is tilted through less than 10 degrees. As soon as the specimen is tilted through an angle greater than 10 deg., a different calibration curve is applicable as you suggest.

V. Thien: What is the reason to measure Z, when EDX/WDX systems are better tools?

Author: EDX and WDX analytical techniques are not able to solve a lot of problems. There are problems such as peak overlap, e.g., O and Cr, Pb, Mo and S; detection of light elements e.g., Li, Be and N and variations in the amount of water of hydration, that are not easily solved by existing techniques. This provides an additional tool that researchers can use to help solve some of these problems. It does not replace these techniques, instead, it can work with them to provide further information about the specimen.

M.G. Hall: It should be borne in mind that, far from yielding no information as to the chemical composition of oxides, carbides, nitrides and other new compounds containing the 'light' elements, EDS analysis is capable of determining the composition of such compounds with some accuracy. Reed and Ware (J. Petrol. 16, II, 499-519) have clearly shown that the chemical composition of a large number of complex silicate minerals can be determined to a relative accuracy of at worst + 2% for the analysis of FeO, SiO₂, MgO, CuO, Na₂O, K₂O, etc. in cases either where the valence state of the cation is known or where a standardized beam intensity is used. We have used this technique for a wide range of compounds with similar success. I doubt if such precision could be obtained with the technique described here, particularly in view of the uncertainties involved in describing the electron back-scattering process. Independent techniques, such as these, possibly also using a windowless X-ray detector, should always be used to check the results of quantitative back-scattered electron signal measurements, if possible.

Author: Thank you for your comments.

Editor's addition (based on a review):

This procedure is not entirely new. The basis for it is described (although with a different detector) in a reference:

Heinrich KFJ (1966) Electron probe microanalysis by specimen current measurement, in: X-ray Optics and Microanalysis (Eds) R. Castaing, P. Deschamps, J. Philibert. Hermann, Paris, 159-167.

