

eons

ISI
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NEWS SERVICE

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Quantitative Compositional Microanalysis in a Scanning Electron Microscope.

A new microanalysis technique that uses the backscattered electron signal to analyze specimens according to compound formula provides the ideal complement to x-ray spectroscopy for compositional analysis.

Determination of compounds, especially compounds containing light elements such as H, Li, Be, B, C, N, O and F, has always been a problem in SEM microanalysis. Now, a unique system that takes advantage of the relationship between the average atomic number (AAN) of elements in a specimen and the energy of the backscattered electrons they generate when struck by high energy electron beam, makes *compound* determination possible for the first time.

Historical Perspective

In the past, compositional analysis of specimens has been performed by a variety of methods. Before 1950, the majority of quantitative analyses were done by "wet" chemical methods in which the sample was first dissolved, then the insoluble compounds were precipitated out and weighed. The obvious drawback to this method was that the specimen being analyzed had to be relatively free of impurities and it was frequently difficult, if not impossible, to isolate enough pure material for analysis.

With the introduction of the electron microprobe, and more recently the scanning electron microscope (SEM), it became possible to perform quantitative analysis *in situ*, on areas as small as 1 micron in diameter. As a result, a number of analytical methods were developed for use in the SEM, the most common of which are wavelength dispersive x-ray spectrometry (WDS) and energy dispersive x-ray spectrometry (EDS), with EDS being by far the most popular.

Since the introduction of x-ray microanalysis methods, many improvements and advancements have been made in x-ray microanalysis instrumentation, spectrum processing, and data analysis techniques. However, a number of limitations remain. Most notably, from the standpoint of compositional analysis, these are that x-ray spectrometry cannot detect elements below a certain atomic number (typically, $Z = 4$ for WDS and $Z = 9$ for

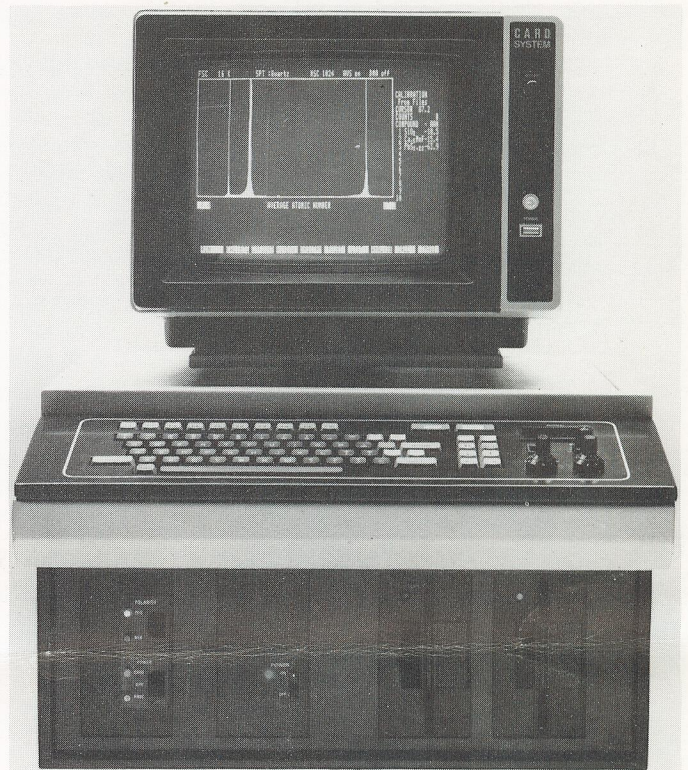


Figure 1. The CARD system includes an atomic number sensitive retractable Robinson backscattered electron detector (not shown), a microprocessor based multichannel analyzer, a color display terminal, a dual floppy disk drive, and complete software for identifying compounds and performing calculations. It can be attached to any SEM.

EDS with a beryllium window detector), and it cannot determine the oxidation state of elements, or the presence or absence of H_2O , without introducing the possibility of considerable error. In many applications, these restrictions are cause for concern.

Compositional Analysis with a Robinson Detector (CARD for short) introduces an entirely new concept in microanalysis. It offers a rapid method of obtaining quantitative information about the chemical composition of a wide range of compounds, identifies many compounds including those which contain light elements and water of hydration, and determines the percentage of each compound within a field of view.

Operating Principles

Compositional analysis operates on the principles associated with backscattered electron (BSE) imaging. When a high energy electron beam strikes a specimen surface, a fraction of the incident electrons are scattered back out of the specimen. The number of these backscattered electrons depends on the surface topography, atomic number, crystallographic orientation, and internal magnetic and electrical fields. Internal electrical fields are eliminated in any specimen that is conducting or has an

In this issue of EONS

Last April, at the SEM, Inc. meeting in Dearborn, Michigan, ISI introduced a new microanalysis technique that enables an SEM operator to quickly and accurately analyze the composition of compounds by their chemical formula. The new system is called CARD, short for Compositional Analysis with a Robinson Detector. Because of the interest generated by the CARD system, this special issue of *EONS* is devoted entirely to an article that describes the new CARD system, including examples of how it works. After you have had a chance to look over the article, please don't hesitate to call ISI to find out more about the CARD system. Also, make a note to see the CARD system in operation at the upcoming EMSA meeting in Phoenix, Arizona, August 8-11, Booths 22-25.

electrically discharging surface (i.e., coated specimens or specimens surrounded by gas molecules in a vacuum). Crystallographic orientation effects are integrated and almost completely averaged out when beam convergence exceeds about 5×10^{-3} radian. Magnetic field effects apply to very few specimens, and can be ignored in most cases. And, after eliminating or suppressing the topography component, the backscattered electron signal depends only on the average atomic number of the specimen.

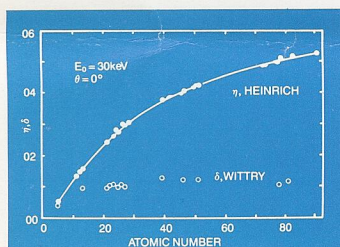
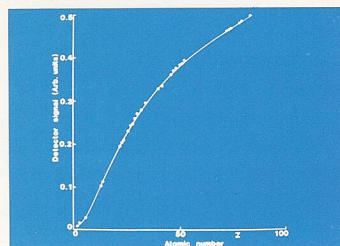


Figure 2. a) backscattered electron yield as a monotonically increasing function of atomic number.



b) Variation of signal output from a BSE detector with respect to atomic number.

The variation of backscattered electron yield is a monotonically increasing function of atomic number as shown in Figure 2, curve a. Figure 2 curve b shows the variation of signal output from a backscattered electron detector with respect to atomic number.

The difference between curve a and curve b is due to three factors: (a) the number and direction of backscattered electrons detected, (b) the energy of the backscattered electrons detected, and (c) the efficiency of the backscatter electron detector. The shape of the detector and its distance from the specimen determines the solid angle subtended by the detector, which in turn determines the number of backscattered electrons detected. The energy of the backscattered electrons is determined by the energy of the incident beam and the atomic number of the sample. The detection efficiency of the detector is determined by the energy of the backscattered electron, the material from which

the detector is constructed, and the gain of the amplification system.

The CARD system uses a specially designed, atomic number sensitive, retractable Robinson backscattered electron detector and a microprocessor-based analyzer that contains its own unique curve for backscattered electron signal versus atomic number (Figure 2.b). This curve applies to both pure elements and compounds. The computer also uses its own formula for calculating the average atomic number of a compound from the combination of atomic numbers of all the elements present in the compound.

To use CARD, all an operator has to do is load the system software, calibrate and run. Calibration consists of measuring the backscattered electron signal from two known reference elements. The system is then calibrated for those operating parameters and will remain calibrated as long as those parameters do not change.

In point analysis, CARD instantly provides the average atomic number (AAN) of the point under investigation. With the addition of other information about the elements present, as determined by EDS for example, CARD can reference a compound library contained on disk and display the possible compounds containing those elements, taking into account the presence of light elements, water of hydration, etc.

CARD also performs area analysis. When an area containing a number of different compounds is scanned, CARD produces a spectrum consisting of peaks for each compound present. The area under each peak is proportional to the area occupied by that particular phase in the specimen. Using a cursor, the operator can identify each compound by its AAN, calculate the area of each peak, and determine the percent concentration of each phase within the field of view — all in a matter of minutes.

Applications

The CARD system has tremendous application potential in areas where it is necessary to differentiate the possible compounds contained in a specimen, such as is often required in mineralogy, geology, and materials science. In these areas and others like them, CARD will be used to detect the presence of compounds and calculate their status.

Many CARD applications will be in conjunction with EDS. In most cases, a qualitative EDS system will be sufficient, since its main function will be to provide elemental information. This combination (EDS & CARD), for most applications, will give the same results as fully quantitative EDS or EDS and WDS combined, only it will do it in a fraction of the time.

In some instances, the number of compounds that need to be differentiated is limited and all of them are known. This occurs, for example, when studying samples from a region of known mineralogical properties and when monitoring the formation of nitrides, hydrides, oxides, etc., of known elements during production processes. Under these and similar circumstances, CARD alone gives positive phase identification.

The following examples are provided to illustrate the use of the CARD system in solving specimen composition problems.

EXAMPLE 1

A sample of sheet steel was studied to determine the cause of differences in surface appearance suspected to be due to changes in phosphorous content (see Figure 3). An SEM backscattered electron (BSE) image of the specimen identified two phases, a dark phase (phase A) and a light grey phase (phase B). Further, phase A was seen to contain a bright matrix material with a darker material finely dispersed throughout (Figure 4).

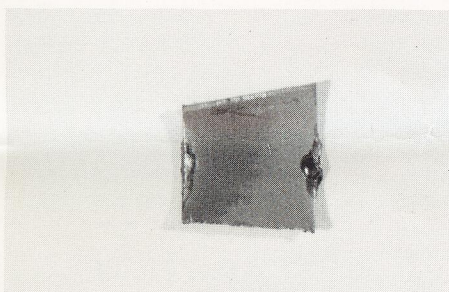


Figure 3. Photograph of specimen.

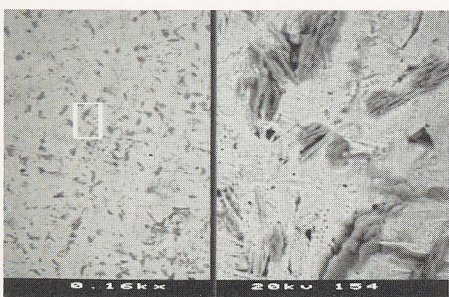


Figure 4. Dark grey side (phase A). 160×/1600× BSE micrograph.

EDS analysis of phase A shows the bright matrix material contains predominantly Fe, with small amounts of P and Na (Figure 5). CARD analysis determines that the bright matrix material has an AAN of 23.9 (Figure 6).

If only Fe and P were present, approximately one P atom would be required for every two Fe atoms (i.e., Fe_2P) to take Fe ($Z = 26$) down to an

AAN of 23.8. However, the EDS analysis indicates only a small amount of P is present, not nearly enough to combine with Fe in a 1:2 ratio.

CARD provides the answer. Fe present as 5% $\text{Fe}_3(\text{PO}_4)_2$ in solid solution would lower the AAN from 26 to 23.9 and would show only a small amount of P on the EDS spectrum.

The dark material dispersed in the bright matrix material was analyzed next. EDS shows it contains strong Fe and P peaks with smaller Zn and Na peaks (Figure 7). CARD analysis indicates an AAN of approximately 17 to 18.5 (Figure 8). $\text{Fe}_3(\text{PO}_4)_2$ has an AAN of 17.1 and $\text{Zn}_3(\text{PO}_4)_2$ has an AAN of 19.3. A CARD peak in the range from 17 to 18.5 AAN, along with varying amounts of Fe and Zn indicates a mixture of these two compounds.

It is concluded that the dark material (10% by area) dispersed in the bright matrix is a mixture of $\text{Fe}_3(\text{PO}_4)_2$ and $\text{Zn}(\text{PO}_4)_2$ with small amounts of Na.

The light grey side (phase B) of the sample was also examined, and the BSE image (Figure 9) indicated that it consisted of the same bright matrix material (5% $\text{Fe}_3(\text{PO}_4)_2$ in solid solution) with a heavier concentration of the dark $\text{Fe}_3(\text{PO}_4)_2$ material (50% by area).

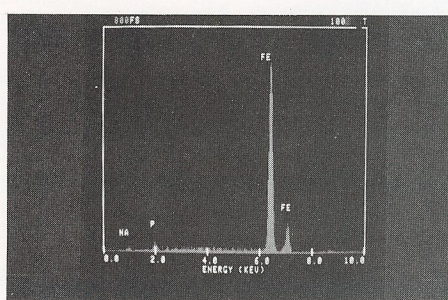


Figure 5. EDS analysis of bright matrix in phase A.

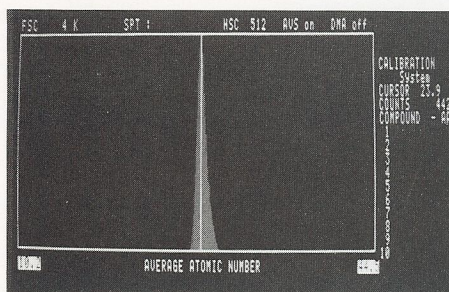


Figure 6. CARD analysis of bright matrix material in phase A.

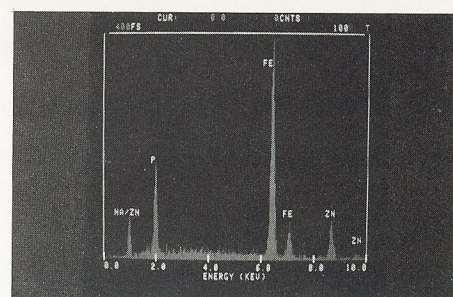


Figure 7. EDS analysis of dark phase dispersed in bright matrix.

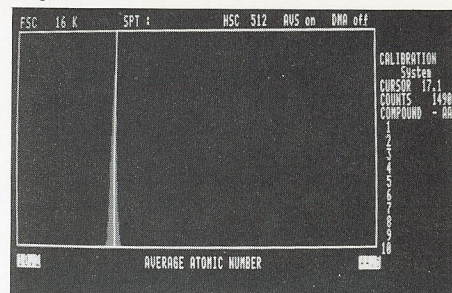


Figure 8. CARD analysis of dark phase dispersed in bright matrix.

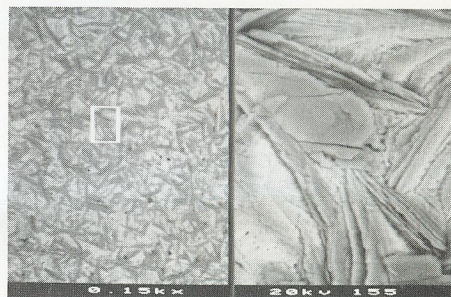


Figure 9. BSE micrograph, light grey side (phase B). 150×/1500×.

EXAMPLE 2

In this example the material under investigation was a mineral with three distinct phases. The problem was to identify the compound composition of each phase.

The BSE image (Figure 10) clearly shows three phases, in increasing atomic number, black, grey and white. (We will ignore the small amount of light grey phase in the center of the micrograph.)

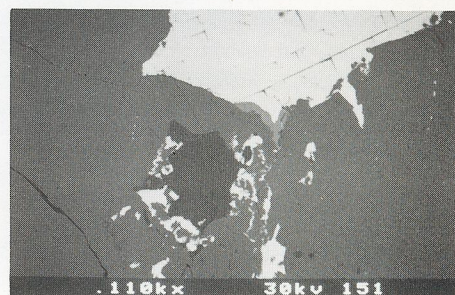


Figure 10. BSE micrograph of specimen.

The CARD spectrum (Figure 11), taken simultaneously with the BSE micrograph, shows three peaks, in order of increasing atomic number (from left to right), corresponding to the black, grey and white phases.

EDS analysis of the black phase (Figure 12a) indicates the presence of Si only (Z = 14). However, the CARD system shows the peak has an AAN of 10.5 which indicates that the Si is tied up with a light element. Upon interrogation, CARD tells us that at an AAN of 10.5 Si would have to be present with oxygen as SiO₂ and lists the compound on the right-hand side of the display (Figure 11) as 1.SiO₂-10.5.

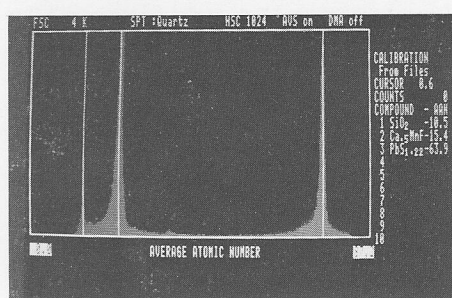


Figure 11. CARD analysis of specimen.

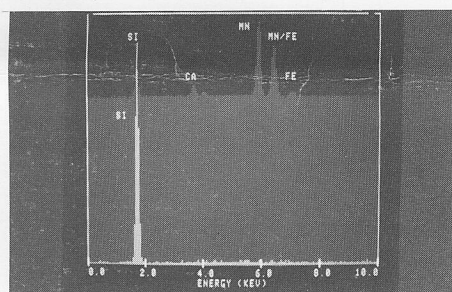


Figure 12. a) EDS analysis of black phase, note Si peak. b) EDS analysis of grey phase, note presence of Si, Ca, Mn, and Fe.

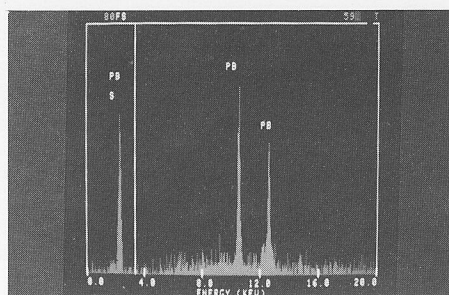


Figure 13. EDS analysis of white phase showing presence of Pb and S.

EDS analysis of the grey phase (Figure 12b) indicates the presence of Mn (Z = 25), Fe (Z = 26), Ca (Z = 20), Si (Z = 14). CARD analysis shows a peak at an AAN of 15.4 which, once again, tells us that light elements are present. Upon further interrogation, CARD tells us that the correct compound for an AAN of 15.4 is Ca₅MnFe₂(SiO₃)₄ and once again lists the compound and its AAN on the right-hand side of the display.

We now go to the white phase. EDS (Figure 13) indicates the presence of Pb and S with a severe overlap problem. CARD indicates a peak at an AAN of 63.9. If PbS was present, the AAN would be 66.4. The difference between 66.4 and 63.9 is not large enough to accommodate the presence of any light elements. However, we know that Pb and S go into solid solution from PbS to PbS₂. With the CARD ratio routine, we can determine the specific stoichiometry for Pb and S with an AAN of 63.9. CARD tells us the correct formula is PbS_{1.224}.

The CARD system has now successfully determined the compound formula of each phase. Now we use it

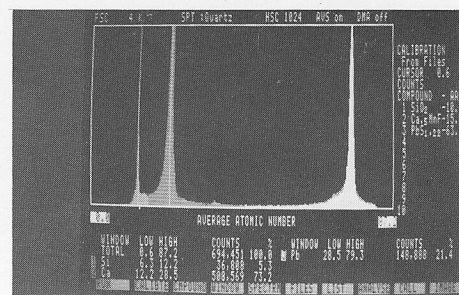


Figure 14. CARD analysis of percent area occupied by each phase within the field of view.

to tell us what percentage of each phase is present in the BSE image. Using the window routine (Figure 14) CARD provides the following information: peak 1. SiO₂ = 5.3%; peak 2. Ca₅MnFe₂(SiO₃)₄ = 73.2%; and peak 3. PbS_{1.224} = 21.4%.

In these, and other examples like them, CARD is the only micro-analytical technique that can provide the compositional analysis capability that is often required.

ISI has compiled a number of application examples, such as these shown here that illustrate the use of the CARD system. For more information concerning CARD, contact ISI at (408) 727-9840.

ISI is currently soliciting samples for CARD analysis. If you have samples you would like to submit contact Bob Ruscica at the ISI number given above. ISI asks that all samples submitted be mounted in a one-inch mount and prepared as they would be for quantitative microanalysis (i.e., polished). In addition, please include any information about the samples you may have such as their origin and possible compound composition.

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