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ABSTRACT

THE ELECTRON MICROPROBE FOR CHEMICAL ANALYSIS

by
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The electron microprobe is extremely useful in determining the qualitative and quantitative analysis of areas of micron-size diameter. By means of a finely focused electron beam, the x-ray fluorescence analysis of selected areas may be obtained. Recent advances in techniques and equipment permit analyses of elements below magnesium in the periodic table. The correction procedures necessary for application to the raw data will be discussed. The results obtained by the detection of back-scattered electrons and by characteristic x-ray emission will be presented, illustrating other applications of the microprobe. Examples of analyses to detect homogeneous or inhomogeneous mixtures, the distribution of phases within a matrix, and the diffusion of elements also will be discussed.

THE ELECTRON MICROPROBE FOR CHEMICAL ANALYSIS

Introduction

Electron probe x-ray fluorescence analysis is a relatively new analytical method for chemical analysis, permitting the determination of the constituents in a minute, localized volume. This is a most significant advance in analytical techniques, and it is also a nondestructive method of analyzing areas at the surface of solid specimens. The application of this instrument to phase diagram studies, to diffusion measurements, to studies of segregation, and the analysis of precipitates has been reported in many instances, and additional reports are being published in almost every journal. This paper is intended to include a general description of one instrument, plus a review of some analytical procedures and examples of applications of the probe.

The complete instrument (Figure 1) is relatively large, requiring sensitive controls and numerous electronic components. However, the critical portion is the finely focused beam of electrons which is directed at the specimen surface to a particular area of interest. The electron beam, which may be less than one micron in diameter, excites an x-ray spectrum containing the characteristic wavelengths of the elements in the microconstituent volume. The intensities of the characteristic wavelengths are related to the mass concentration of the particular elements. Specific crystals are used to diffract the x-rays into the component wavelengths, and the selected rays are then focused to appropriate detectors. By determining the characteristic wavelength emitted by the specimen, one can analyze qualitatively the elements present, and, by determining the intensity of the detected rays, one can obtain a quantitative analysis of the element producing the x-rays. The volume being analyzed is on the order of 10^{-12} cubic centimeters. Depending upon the element analyzed, the matrix, and the beam spot size, the sensitivity of the method ranges from 0.1% down to 0.001%, with a relative accuracy of 0.1% for elements with atomic numbers above eleven. Recent improvements have enabled the experimenter to analyze elements down to atomic number 4, which includes boron, carbon, oxygen, and nitrogen, though with less sensitivity than for elements of higher atomic number.

The Electron Microprobe

Due to the number of manufacturers of electron probe instruments, certain design characteristics are different for the different instruments. Such variations occur in the electron optics system, the design of the electron lens, the take-off angle, the optical viewing arrangement, and the specimen movement. This paper will be devoted to describing only the one particular instrument used in the Materials Research and Development Branch, Goddard Space Flight Center, rather than comparing different instruments.

The electrons are emitted from a tungsten wire filament, and by a voltage biasing arrangement the electrons pass through an aperture and toward the sample. The electrons are collimated into a beam and are directed and controlled by the magnetic condenser lens and the magnetic objective lens. Two fluorescent screens may be moved into the path of the electron beam so that the beam configuration may be maximized using the magnetic lenses. The diameter of the electron beam at the surface of the specimen is continuously adjustable from about 0.3 micron to 300 microns. The point at which the beam strikes the surface can be observed visually through a light optical system.

The electron beam causes the characteristic x-rays to be emitted by the elements; the excitation is detected and analyzed by the monochromator which consists of a crystal, receiving slits, and a detector. These are all within the vacuum system, and adjustments to the crystal and to the detector can be made from outside the tank.

The crystals are the means by which the radiation from the specimen is diffracted and focused to the detector. The crystals are ground to either a 4" or 11" radius. Typical crystals and the wavelength range of analysis for a 4" radius of the focal circle may include the following:

Crystal	Wavelength Range
LiF	1.00A- 3.77A
NaCl	1.41A- 5.29A
SiO_2	1.67A- 6.26A
ADP	2.66A-10.00A

The K-alpha emission line for magnesium (atomic number 12) is 9.889A and for titanium (atomic number 22) is 2.748A, which indicates the possible range for the ADP crystal. The K-alpha emission line for potassium (number 19) is 3.741A and for bromine (number 35) is 1.039A which gives an indication of the range of elements for the LiF crystal. However, the elements of higher atomic number can be analyzed with these same crystals by determining the L- and M-alpha emissions; for example, the L-alpha wavelength of arsenic (number 33) is 9.7A and that for bismuth (number 83) is 1.14A. Elements such as dysprosium (number 66) up to uranium (number 92) can be detected with the above crystals by the presence of the M-alpha lines which would range from 9.5A for dysprosium to 3.9A for uranium.

For elements having atomic numbers lower than magnesium, the very long wavelengths of the K-alpha lines require other crystals. The analysis of aluminum (number 13) with a wavelength of 8.339A and of oxygen (number 8) with its wavelength of 23.5A can be done with the KAP crystal. With a lead stearate crystal, nitrogen (number 7) with a wavelength of 31.2A and boron (number 5) with a wavelength of 64.5A can be detected.

Under normal operating conditions the separation of the elemental K-alpha, and the K-alpha$_2$ line can be detected and recorded, as for nickel in which this separation is only 0.003A. The important criterion of operating efficiency is the line-to-background ratio which should be as large as possible, and this ratio often exceeds a value of 300 for elements of high concentration.

The line-to-background ratio can be utilized in estimating the limit of detection of an element, as mentioned by Birks[1]. Using copper as an example, the line-to-background ratio for the copper K-alpha line at an excitation potential of 40 k.e.v. is theoretically 3000/1, but due to crystal imperfections, scattered radiation, and geometry of the crystal arrangement, this ratio is reduced to about 1100/1 for a lithium fluoride crystal. As the percentage of the analyzed element becomes less, the line-to-background ratio is reduced, and gradually the peak becomes indistinguishable from the background. A common definition for the point at which this occurs is

$$N_L - N_B = 3\sqrt{N_B}$$

or the difference between counts for line and for background is 3 times the standard deviation of the background. With a 3000/1 ratio for pure copper and choosing N_B as 1000, this would give $N_L - N_B \approx 100$. At the 3000/1 ratio, the total counts for copper would be 3,000,000, and the amount observed would be 100/3,000,000 or about 30 p.p.m. Using the 1100/1 ratio of actual practice for the LiF crystal, one might expect to detect a limit of about 100 p.p.m. for copper.

The read-out from the detectors may be by means of a strip-chart recorder, which is a most useful technique in the qualitative analysis for elements. The detectors may be set at the characteristic wavelength of the element known or expected to be present, or else the detector may be changed by hand or automatically driven to search for the increased intensity indicating the presence of an element. Thus one could select a particular area of interest and by using the stationary electron beam

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[1] L. S. Birks, "Electron Probe Microanalysis", Interscience Publishers, 1963, p. 136.

manually or automatically cycle the x-ray monochromators through the spectrum for that crystal, each of the three detectors of the instrument being used concurrently so as to cover the full wavelength range; a deflection of the pen on the strip chart occurs at a characteristic wavelength and indicates the presence of an element. One can also set the x-ray monochromator on a particular wavelength with the specimen being moved manually or automatically along a particular direction; this automatic movement may be done by preselected steps of 1 to 10 microns or at a continuous rate of either 8 or 96 microns per minute. One can also correlate the step-like motion with the recorder chart movement and with optical observation of the specimen to determine the areas of irregular or notable elemental content, as would occur for a precipitate.

In addition to the spot determination, we are able to cover a much larger area by scanning. Within the area of the specimen are a set of four electrostatic deflection plates with a similar set of deflection plates located in the oscilloscope. These two sets of four plates are synchronized so that a sweep voltage applied to the X axis will control the scanning rate and a sweep voltage applied to the Y axis plates gives the number of lines per frame. In this way a picture representing what one sees optically can be presented on the oscilloscope by means of back-scattered electrons from the specimen. This display on the oscilloscope gives a general indication of how the elements are distributed within the specimen and also the presence of imperfections, such as holes. This also results in a discrimination between elements since the elements of higher atomic number will "back scatter" more electrons from the specimen surface and will result in brighter areas on the oscilloscope screen. Thus, the brightest areas indicate higher atomic number elements, and the less bright or greyish areas are the lower atomic number elements, while black areas are still lower atomic number elements or may be holes. This display system is extremely useful, as later photographs will show. The nominal deflection of the electron beam in the scanning mode is 360 microns; magnification of the area can be accomplished by reducing the deflections in the X and the Y axes by factors of 1/2, 1/4, or 1/8.

Rather than using the strip-chart recorder to determine the relative amount of each element present, a more sensitive and accurate way is by counting the pulses picked up by the monochromator at a particular wavelength. In this instrument each of the detectors may be set on a selected wavelength and in a fixed-time mode the total counts will appear on the three indicators, with the counting being stopped automatically after the preselected time. These numbers thus obtained form the basis for the quantitative calculations.

Quantitative Considerations

The calculation of the elemental content of a selected area of a specimen begins with the determination of the number of pulses received in a selected time, but these numbers must be corrected for effects due to the specimen and to the detector. Two particular corrections are for detector dead-time and for the background.

Dead-time is a function of the pulse-detecting system, and a correction must be applied to the apparent number of pulses or counts. Dead-time results when the detector is unable to keep up with a high rate of counting and results in a detector being saturated. Such a high counting rate occurs most often with relatively pure samples when the rate is on the order of 14,000 counts per second for this particular instrument.

The background correction is determined by selecting a wavelength adjacent to the wavelength of interest for a particular element and determining the pulses arising from scattering, bremsstrahlung, or general electronic "noise". This background correction becomes increasingly important when the element of interest is present in small amounts, and the resultant peak is not predominantly above background.

Additional corrections are more complicated and more critical and these involve ones due to absorption, to fluorescence, and to a difference in atomic number of the elements present. In striking the surface of the specimen, the electrons penetrate below the surface and as a result some x-rays are generated an appreciable distance below the surface. These x-rays may be absorbed by the specimen before emerging from the surface, thus modifying the x-ray intensity generated within the volume and requiring an absorption correction. Castaing[2] developed a theoretical model and also derived some experimental curves which permits the determining of an absorption correction factor.

It is also possible that the characteristic radiation of an element in a binary alloy has the energy to excite the characteristic radiation of the other element by fluorescence. As an example, we can consider an alloy of nickel and iron. A correction has to be made for the absorption of the nickel radiation by the iron, and a correction must be made for the fluorescence radiation from iron by nickel because the Ni K-alpha radiation is a shorter wavelength than the K absorption edge of iron. Castaing also developed an expression for the fractional increase in K-alpha intensity in element A which is produced by the K-alpha

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[2] R. Castaing, "Advance in Electronics and Electron Physics", vol. XIII, p. 317, Academic Press, 1960.

radiation from element B. Wittry[3] developed improved correction procedures and presented the parameters in graphical form. The formula is limited to cases where K radiation is excited by other K radiation.

The effect of a difference in atomic number between the components in an alloy has been considered by Archard and Mulvey[4] utilizing a simplified theoretical model of the electron interactions within a solid. The expressions derived by them require a considerable amount of computations, and they conclude that "although the atomic number effect is small for neighboring elements such as Cu - Zn, it may be quite large for neighboring elements such as Cu - Ni, which differ markedly in their values of Z/A".

The results of a series of calculations by Poole and Thomas[5] will serve to indicate the effect of various corrections upon the data from an electron probe. A few selected results will show the accuracy of the analyses. In analyzing for gold in a copper-gold alloy known to contain 23.8% gold, the results of applying increasingly better correction procedures to the raw data resulted in estimated concentrations of 17.4, 19.9, 21.4, 25.2, and 23.5% gold. These results gave an error ranging from -27% to +5.9%. In another instance in which the element estimated is copper in a copper-aluminum alloy containing 53.6% copper, the microprobe results with the various corrections gave values of 49.6, 49.6, 51.0, 54.6, and 53.6% copper. The range of error for these results was -7.5% to +1.8%.

In additional computations by Ziebold and Ogilvie[6], a similar series of analyses and calculations were made. The results of these calculations were not complete due to a lack of mass absorption coefficients for long wavelength lines in heavy elements and in trying to compute fluorescence for L lines for which certain physical properties are not well known. These authors achieved results of better than 5% accuracy, but they also concluded that "accurate measurements require the use of carefully prepared calibration standards to convert x-ray data to mass compositions. These standards must be chemically homogeneous on a

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[3] D. B. Wittry, U.S. AEC Report 84-204, U. of Southern California, (1962).

[4] G. D. Archard and T. Mulvey, "The Effect of Atomic Number in X-ray Microanalysis", International Symposium on X-ray Optics and X-ray Microanalysis, Stanford Univ., 1962.

[5] D. M. Poole and P. M. Thomas, "Quantitative Electron-Probe Microanalysis", J. Inst. Metals, 90, 228-233, 1961-62.

[6] T. O. Ziebold and R. E. Ogilvie, "Quantitative Analysis with the Electron Microanalyzer", Anal. Chem., 35, #6, 621-627 (1963).

microscopic scale, and the calibration curves must be measured many times to establish their degree of reproducibility. By this approach one should obtain measurements having 2% or better accuracy."

The procedures and corrections mentioned above indicate that for a multi-component alloy a considerable number of calculations would be required. The obvious next step is to utilize a computer for making corrections to the data. Fortunately, a number of experimenters have developed computer programs to take over this task. However, the computers provide speed only and their results are no better than the correction procedures available. Much remains to be done in providing theoretical and experimental results to enable one to determine the concentration of an element within a specimen.

Experimental Observations

One major advantage of the electron probe is in providing a microscopic view of the specimen. This enables the operator to note areas of particular interest, as areas where reactions are occurring.

One example is the reaction of zinc with ruthenium, in which the ruthenium was kept in molten zinc to permit any reaction to occur. We found that the $RuZn_9$ compound is formed and that the zinc penetrates along the ruthenium grain boundaries to form the compound. The apperance of the specimen as viewed by the operator through the optical system is shown in Figure 2. The same area is delineated by means of the back-scattered electrons, as shown in Figure 3, in which the ruthenium areas are lighter in appearance. The use of zinc characteristic x-rays produces the opposite contrast, Figure 4, in which the zinc-rich areas are the light areas.

A similar sample was formed by reacting zinc with rhodium, and though ruthenium and rhodium are adjacent in the periodic table, being atomic number 44 and 45, respectively, yet the electron probe shows that a number of intermetallic compounds are formed between rhodium and zinc. The photograph of the specimen shows a particular greyish area adjacent to the light-colored rhodium, Figure 5. This outer band is indicative of the probable formation of one or more intermetallic compounds in this system. By employing the combination of the back-scattered electrons and the trace of the probe across the center of the picture we can show how the zinc and the rhodium content vary. The uppermost trace in Figure 6 shows the change of zinc content as the electron beam crosses the edge of the dark, round area and then into the dark area; the zinc content is relatively high in these dark areas. The lowest trace indicates the relative rhodium content; in the dark circular area the rhodium content decreases while the zinc content is high, and in the light area the rhodium content is at a high level. At the interface between the zinc and the rhodium, the rhodium trace drops in two steps to a relatively long plateau after which it drops again to the lowest percentage. The trace thus indicates that two or possibly three compounds are formed.

Another example of the usefulness of the electron probe is shown in Figures 7 and 8, in which the interface between an iron shoe, a tin-tellurium braze, and a lead telluride thermoelectric element is shown. The back-scatter picture outlines the areas of high and low atomic number elements. The trace of the electron beam shows the percentages of iron, tin, and tellurium in the different areas.

The above results showing the reactions between the elements and showing the distribution of elements within a solid specimen indicates some applications of the electron probe. Despite a relatively large error in quantitative analyses due to inadequate correction procedures, the electron probe is adaptable to numerous analyses involving surface reactions, diffusion, and the detection of inhomogeneous areas.

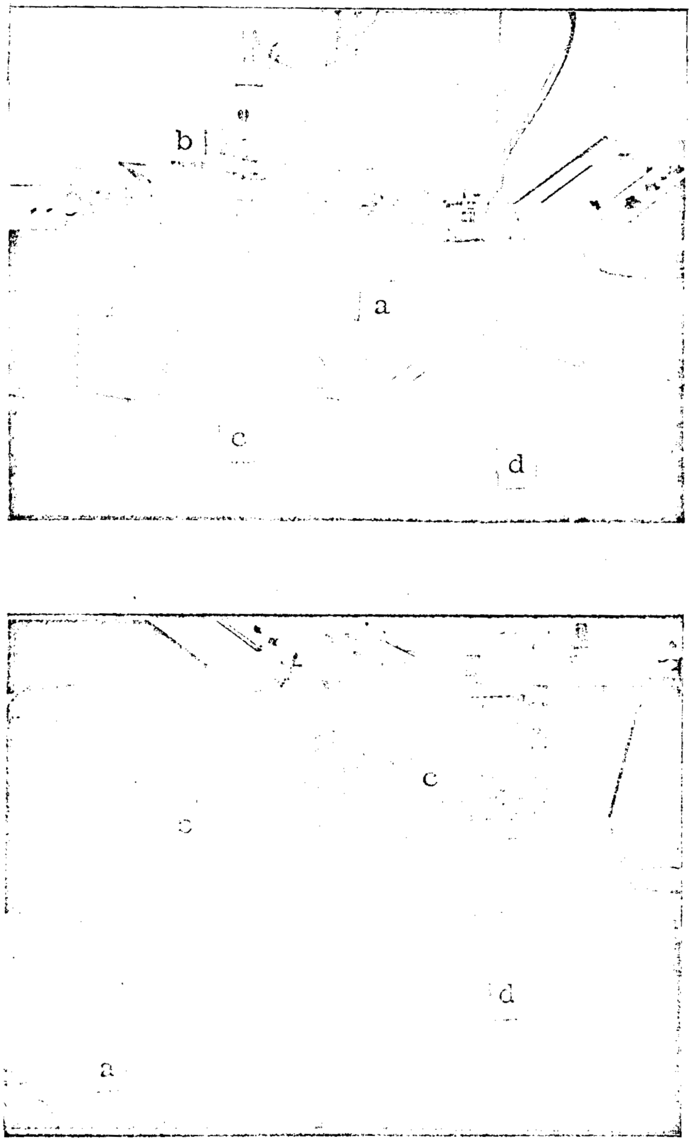

Figure 1. Electron Microprobe Instrument
A. Probe vacuum chamber and controls:
a - Vacuum tank; b - Filament location; c - Sample chamber; d - Filament and lens controls.
B. Probe Read-out System: a - Automatic typewriter; b - Numerical read-out; c - Oscilloscope display; d - Electron back scatter controls.

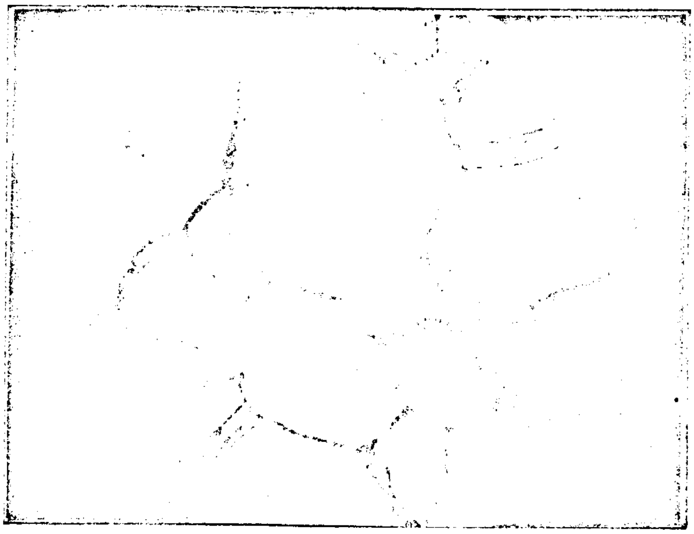

Figure 2. Ruthenium-zinc Alloy.
Optical view of $RuZn_9$ compound formed in the ruthenium grain boundaries. Unetched. x 280.

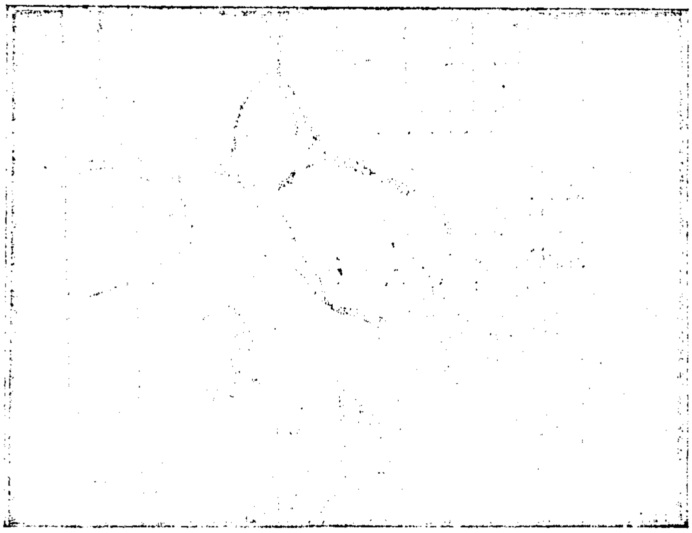

Figure 3. Ruthenium-zinc Alloy.
Electron back scatter display. Light areas are ruthenium-rich and dark areas are zinc-rich. x 222.

Figure 4. Ruthenium-zinc Alloy.
Zinc X-ray display, with zinc-rich areas appearing light in color and ruthenium-rich areas appearing dark. x 222.

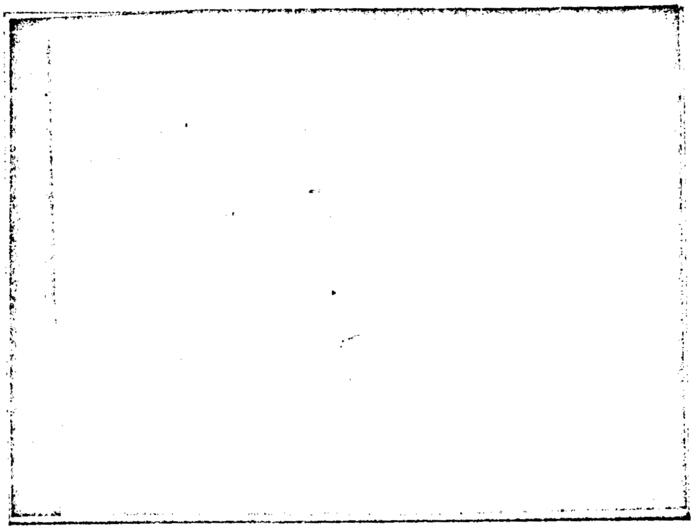

Figure 5. Rhodium-zinc Alloy.
Electron back scatter display of reacted materials with rhodium-rich areas appearing light and zinc-rich areas appearing dark. Reaction zone at edge of rhodium is greyish and hole in rhodium shows presence of zinc. x 222.

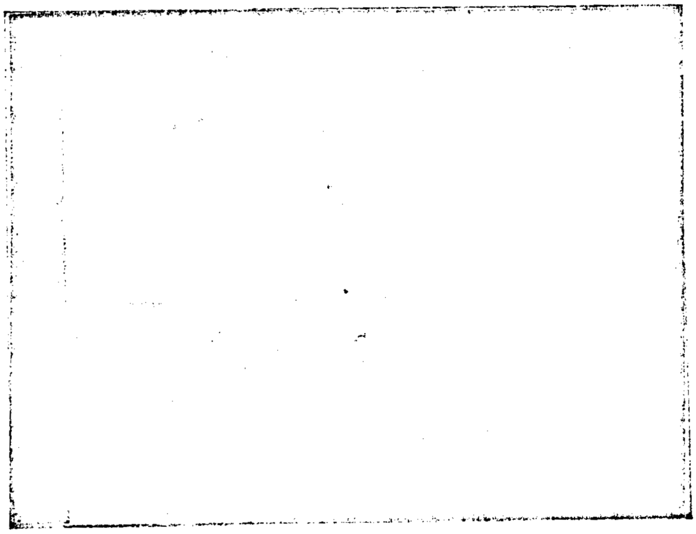

Figure 6. Rhodium-zinc Alloy.
Zinc content is indicated by top white line and rhodium content by bottom white line. Central white line is area of electron probe trace. x222.

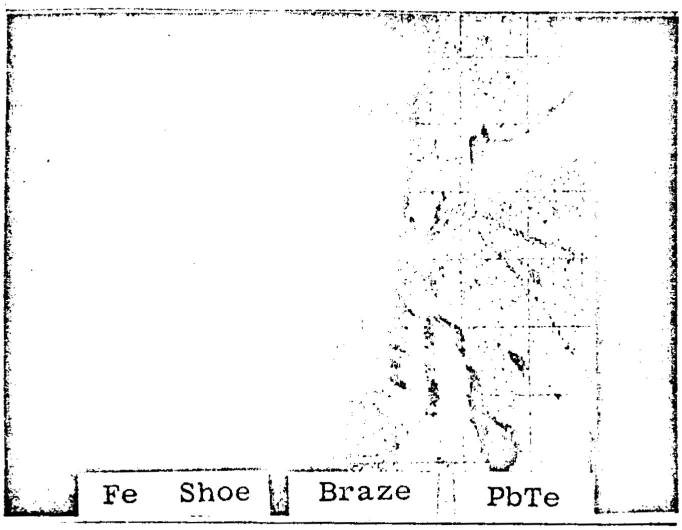

Figure 7. Brazing of Iron to Lead Telluride. Electron back scatter display of iron shoe (dark), tin-tellurium braze (grey), and lead telluride element (white). x 222.

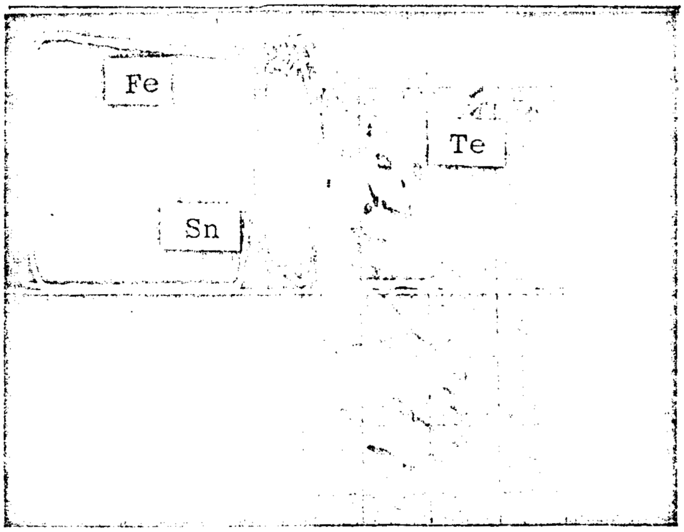

Figure 8. Brazing of Iron to Lead Telluride. X-ray traces of iron, tin, and tellurium contents across braze area. Electron beam passed along central white line.