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THE APPLICATION OF TWO DIMENSIONAL SCANNING TO LIGHT ELEMENT MAPPING WITH THE NUCLEAR MICROPROBE

T.B. Pierce and J. Huddleston

Abstract

Elemental distributions have been obtained for a number of samples during application of the nuclear microprobe, by photographically recording the output of an oscilloscope operating in sequence with the ion beam during electrostatic deflection. The technique has been found to complement the point-by-point method of sample interrogation which is now in regular use. Nuclear reactions provide information about light elements and X-rays, about elements of heavier atomic number. The technique is illustrated by maps for boron, carbon, nitrogen, oxygen, chromium and iron which have been obtained for particular samples.

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1. Introduction

The nuclear microprobe is now established as a method of determining the spatial distribution of light elements⁽¹⁾. The technique is based on measurement of the prompt radiation emitted during charged-particle irradiation and ion energies are chosen to produce nuclear reactions with nuclei of low atomic number without generating radiation from heavier elements which may comprise the matrix; this simplifies demands made on spectral interpretation. For some applications, X-ray yields are compared with the intensity of radiation produced from nuclear reactions to provide a correlation between light and heavy elements. When quantitative results are needed, counts from nuclear reactions can be interpolated on a calibration curve which has been prepared from irradiation of standard samples.

Past application of the nuclear microprobe has been centred on the generation of line-scans as the ion beam traverses the sample in a single direction. This has permitted quantitative information to be obtained from a range of samples, for example from metals containing carbon⁽²⁾ and nitrogen⁽³⁾ generated by metallurgical and engineering experiments. Line-scans have usually been discontinuous, counting taking place with the beam stationary, and the position of the ion beam on the sample being changed between irradiations. Thus emitted radiation can be related to particular regions on the sample surface. In order to check reproducibility and to confirm the presence of any variations identified within the sample, scans are normally repeated several times and results compared. However, extension of the microprobe to permit the ion-beam to be scanned in two dimensions is attractive to enable the overall trends in elemental distribution to be established and regions of major interest to be identified for more detailed examination. Although two dimensional scanning of the ion beam has already been demonstrated⁽⁴⁾⁽⁵⁾, it has not been applied so far to the determination of the distribution of light elements. In this paper, work is summarised which has been carried out to assess the value of two dimensional scanning for providing a representation of light element distributions and assisting in procedures aimed at more detailed quantitative analysis.

2. Experimental Technique

The configuration of the nuclear microprobe has already been described in detail elsewhere⁽²⁾ and only the main features will be considered here. The microprobe is centred on the 3MV electrostatic generator IBIS at AERE Harwell and the image of the beam on an adjustable stop is focussed on to the target by means of four quadrupole magnets⁽⁶⁾ assembled in the configuration of a Russian quadruplet⁽⁷⁾. The target is secured to the table of the target chamber which can be moved in three dimensions by stepping motors. Charged-particle, X-ray and γ -ray detectors can all be positioned to measure the radiation output of the target during irradiation and detector output is fed by means of the usual amplifying chain to appropriate pulse-height analysing equipment. Single-channel analysers select appropriate pulses for display when scanning is in progress, but signals are also routed to a multi-channel analyser to permit spectral composition to be examined in detail. Deposition of carbon on the sample surface from the accelerator vacuum is reduced by means of a metal finger placed close to the sample surface, cooled by liquid nitrogen. Two microscopes, one in the front and one in the rear of the target chamber permit optical examination of the sample and table. The microscope in the front of the chamber views the face of the

target by means of a drilled mirror positioned in the beam-line, offering line-of-sight down the beam axis. The second microscope enables the shape of the beam on a quartz disc permanently held in the sample table to be examined during setting-up and alignment procedures.

The front microscope is used when samples are initially being positioned with the aid of stepping motors, to ensure that the ion beam falls on the region of interest. Once the sample is correctly positioned, the deflection system is activated so that scanning can commence.

The plates for electrostatic scanning are placed immediately after the quadrupole lenses and consist of two pairs, each driven by a high voltage power supply. The output from the power supply provides a triangular wave-form variable between 0 and 1 kV, with one set of plates being driven at 50 Hz and the other at 500 Hz. Additional outputs from the wave-form generators control the X and Y movements of an oscilloscope. These outputs have a range of 0 to 10 volts irrespective of the value of the high voltage output and this magnification of the image on the oscilloscope is achieved by reducing the area covered by the ion beam raster. The beam conditions selected for imaging are usually governed by a compromise between size and current and the normal conditions are a square spot of about $5\mu\text{m}$ side, providing a beam current of 20 nA. The control system can scan the beam over an area several millimeters square, but areas of interest in this work were very much smaller, less than a millimeter square. Deflection of the ion beam over substantial distances is not attractive since aberrations increase with deflection distance. The output from the radiation detector is fed through a single channel analyser and level changing circuits to the Z input of the oscilloscope.

Samples were mounted in Woods metal and polished with successively finer grades of abrasive to provide a good finish. The Woods metal was contained in an aluminium ring 1-1/8 inch in diameter which fitted precisely into a holder machined in the sample table. A major problem associated with the mounting of samples for light element mapping, particularly if regions near to the edge are to be examined, is the elimination of the effects due to surface films at the interface between sample and mounting material.

One means of eliminating these effects is to copper plate the Woods metal to ensure a good interface between sample and mounting material. The sample is mounted and polished down to $1\mu\text{m}$ diamond by normal methods and then further polished for several minutes with $1\mu\text{m}$ diamond, and a napped cloth under light pressure. This treatment preferentially removes the Woods metal. The sample is then electroplated in an acid copper sulphate bath to produce a copper layer about $5\mu\text{m}$ thick. The copper on the sample is very carefully abraded away with $1\mu\text{m}$ diamond compound and a cloth with very little nap to avoid removing the recessed copper.

The additional polishing inevitably introduces some additional bevelling at the edges, but this can be minimised by carefully controlling the quantity of Woods metal removed.

3. Analytical Methods

Reactions so far applied to analytical measurement with the nuclear microprobe are summarised in Table 1. These are by no means exclusive and many additional reactions emitting prompt radiation have been reported in the open literature which could offer alternative methods of elemental determination. However, those listed have been found to offer convenient solutions to a range of metallurgical problems. The primary object of the work, reported in this paper was to apply two dimensional scanning techniques to generate a visual presentation of the distributions of boron, carbon, nitrogen and oxygen since these elements are the ones most frequently examined with the nuclear microprobe at present. For ease of application when multi-element mapping is required, it is highly desirable that only minimum readjustments to settings of machine and other instrumentation are needed when changing the data presentation from one element to another. For this purpose, deuterons of 1.3 MeV were generally chosen for sample irradiation for all determinations except for those of nitrogen. The energies of particles emitted into the detector from the several elements at this deuteron energy are shown in Table 2, which indicates both the potential and the limitations of the method. Particle-counting was chosen to monitor the progress of nuclear reactions so that the technique could be applied to highly active materials; past experience has shown that acceptable particle spectra were obtained for elements of interest in the types of metallurgical sample most frequently encountered. Table 2 shows that peaks of major intensity from oxygen occur at low energy with carbon, an important minor component in many metallurgical samples, giving rise to a peak at a somewhat higher energy. Boron and nitrogen provide particles of still higher energy which will interfere with each other if both are present in a sample at appreciable concentrations. The relative contributions of the two elements can be distinguished by spectral analysis but complex data manipulation is unlikely to be attractive when the microprobe is being used in high speed scanning mode, because of the demands this imposes on signal handling facilities. Clearly, the effect of the presence of an interference on the presentation of data need only be considered if the extent is such as to affect the overall presentation of the results. In the work reported here, samples fell into two quite distinct categories, high-boron associated with low-nitrogen and vice-versa. Since the spectra from samples was accumulated in a multi-channel pulse-height analyser, it could be carefully analysed to permit the particle peaks to be identified. Absence of interference could thus be confirmed and was assumed to hold over the whole of the matrix scanned since a point-by-point examination of the entire area was impracticable. When the primary purpose of the measurement was to determine nitrogen distributions, the deuteron energy was sometimes increased to 1.9 MeV to improve sensitivity.

Since particles are emitted from oxygen, carbon and boron or nitrogen at the same deuteron energy, there is clearly no need to alter the energy of the incident ion when changing presentations from one of these elements to another. Further, the only adjustment required to the counting system was to route output of the appropriate single channel analyser to the modulation control of the oscilloscope since detector output was usually fed to three single channel analysers set over the oxygen, carbon and boron or nitrogen regions. The technique is therefore convenient to use and enables displays of elemental distributions to be rapidly changed from one element to another. Output from the X-ray detector could

also be fed to the oscilloscope after single channel analysis to provide distributions of heavy elements which could then be correlated with the results found by particle counting.

4. Results

Any two dimensional mapping procedures leading to a visual image representative of some feature of the sample should provide acceptable definition in a comparatively short time. This avoids the need for long data acquisition periods for a procedure which, in many cases, is likely to be supporting more detailed quantitative measurement. It further permits the sample surface to be examined at several points if necessary to gain a more general understanding of sample characteristics, without making undue demands on instrument or operator time. Two dimensional scanning procedures have previously been applied with the microprobe and images were successfully obtained by measurement of elastically scattered particles⁽⁴⁾ and X-rays⁽⁵⁾. In general, however, the X-rays yield produced from major or minor constituents, substantially exceeds that found for the emission of particles from nuclear reactions. An initial requirement was, therefore, to confirm that adequate count rates were obtained from various light elements in specific matrices of interest to provide a satisfactory image. For this purpose, a steel sample containing an inhomogeneous distribution of carbon was first examined since measurement of the distribution of carbon in steel comprises a major part of the workload of the microprobe. The sample contained a diffusion profile due to the migration of carbon into the sample from the edge which had previously been examined quantitatively by the microprobe using the well established line-scan approach. Results were placed on a quantitative basis by interpolating the accumulated count for each point on a calibration curve constructed from measurements obtained from the irradiation of standards. The line-scan profile is given in Figure 1 and shows that the carbon concentration varied from 3.5% at the edge to a lower level of 0.1% near the centre of the sample. The image obtained by accumulating the oscilloscope output for 40 secs is shown in Figure 2 and demonstrates that the carbon gradient can be clearly identified. Exposure time was chosen to permit changes in count rate from the carbon-rich region of the sample to be seen, but a longer exposure, not included in the report, enabled the counts from carbon at the archive level of 0.05% to be recorded. The scanning system was adjusted during this particular investigation to limit examination to the carbon-rich region of the sample edge and the length of the side of each of the graticule squares shown in Figure 2 corresponds to a distance of 70 μm on the sample.

The comparatively high cross section for the $^{12}\text{C}(\text{d},\text{p})^{13}\text{C}$ reaction means that the intensity of the emitted protons from a particular concentration of carbon will be higher than that produced from nitrogen present at similar levels and consequently, a section of a thin sample was examined which contained nitrogen as well as carbon gradients on both surfaces. The nitrogen profile for this sample is given in Figure 3 and the results from scanning the sample are presented in Figure 4; the recorded distributions of the iron K_{α} X-rays, together with protons from carbon and nitrogen are given. Exposures of 10 secs, 20 secs and 60 secs were chosen for the iron, carbon and nitrogen presentations respectively. The iron X-rays define the limits of the steel clearly while the carbon and nitrogen distributions show concentrations of the two light elements along both sample edges with the carbon yield very much greater than that

for nitrogen. Nevertheless, the nitrogen exposure is still adequate to show the regions of nitrogen enrichment. Reproducibility of any scanning system is clearly crucial if the definition offered by the diameter of the incident beam is to be exploited and if the results are to provide a reliable record of actual elemental distributions. Repeat examination of a thin section of steel, again with carbon gradients on both surfaces, is shown in Figure 5 for two irradiations for which exposures were somewhat different, 20 secs and 30 secs. The good repeatability of the various features that are detectable in the data presentation shows that the results are reproducible and compare well.

The considerable difference in take-off angle for particles and X-rays, due to the positioning of the two detectors in the target chamber assembly leads to the need for care in interpretation of data, particularly when the samples cannot be completely surrounded by mounting material. An example of this is given in Figure 6 for a small tube (800 μm outside diameter, wall thickness 100 μm). The chromium and iron presentations due to X-rays show good agreement, as do those for carbon and oxygen found by particle counting but the shapes seen in the two pairs of photographs do not agree. In this case, carbon and oxygen are present as deposits on the internal surface of the tube and the sample is so positioned on the table in the chamber that the particle detector records radiation yields from the deposits some distance down the tube in addition to those on the tube's surface. By moving the ion beam to the other side of the sample, so that the tube and mounting material round the outside of the tube mask any radiation produced within the tube, the results given in Figure 7 were obtained. Iron and chromium distributions are even and of similar form and there is a very slight enrichment of carbon on the inside surface of the tube. However, the most marked feature is the very sharp rise in oxygen concentrations on the internal surface.

The ability of the microprobe to identify boron, carbon and oxygen distributions in the sample is shown in Figure 8 for a weld in which a boron flux has been used. The photograph demonstrates that there are increases in boron and oxygen concentrations in the welded region associated with a corresponding decrease in carbon content. There appears also to be a decrease in iron X-ray yield. The boron results can be compared with the boron autoradiograph given in Figure 9 obtained by recording the α -particles emitted by the $^{10}\text{B}(\text{n},\alpha)^7\text{Li}$ reaction in an insulator. For these results, the sample was contacted with a thin film of cellulose acetobutyrate and sample and insulator irradiated in the reactor DIDO at a flux of 3×10^{12} n/cm²/sec for 1 minute. After the completion of the irradiation, sample and polymer film were removed and separated and the damage trails, left in the detector "developed" with alkali until they became visible under a microscope. The intense penetrating radiations, neutrons and γ -photons, present in the reactor did not damage the cellulose acetobutyrate in any way which interfered with identification of the charged-particle trails. Agreement between the distributions of boron found by two different techniques and given in Figures 8 and 9 is good and confirms the results obtained with the microprobe.

This investigation has shown that two dimensional scanning provides a method of mapping of light element distributions which can be valuable in establishing elemental patterns in many of the types of materials examined routinely with the nuclear microprobe; it is now being introduced into regular use. Since the technique is semi-quantitative, it will in no way replace the quantitative measurements offered

by line-scans, and the two approaches are clearly complementary. The methods are interchangeable since with the appropriate instrumentation, only minimal adjustments are required to move from one technique to the other.

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References

- 1) T.B. Pierce in Characterisation of Solid Surfaces, edited by P.F. Kane and G.R. Larrabee, Plenum Press, New York - London, 1974
- 2) PIERCE, T.B., PECK, P.F., McMILLAN, J.W. and JONES, I.G. Nucl. Instr. Methods, 118 (1974) 115
- 3) OLIVIER, C., McMILLAN, J.W. and PIERCE, T.B. Nucl. Instr. Methods, 124, (1975) 289
- 4) PIERCE, T.B., PECK, P.F. and CUFF, D.R.A. Analyst, 97 (1972) 171
- 5) COOKSON, J.A., FERGUSON, A.T.G., PILLING, F.D. J. Radioanal. Chem., 12 (1972) 39
- 6) COOKSON, J.A. and PILLING, F.D. UKAEA Report AERE-R 6300 (1970)
- 7) DYMNIOV, A.D., FISHKOVA, T. and YAVOR, S. Sov. Phys. - Tech. Phys., 10 (1965) 340

Table 1

Reactions used for Light Element Determinations
with the Nuclear Microprobe

Element	Reaction	Radiation Measured
Lithium	${}^6\text{Li}(d,\alpha){}^4\text{He}$	α
	${}^7\text{Li}(d,\alpha){}^5\text{He}$	α
Beryllium	${}^9\text{Be}(p,\gamma){}^{10}\text{B}$	γ
Boron	${}^{10}\text{B}(d,p){}^{11}\text{B}$	p
	${}^{10}\text{B}(\alpha,p){}^{13}\text{C}$	p
	${}^{11}\text{B}(\alpha,p){}^{14}\text{C}$	p
Carbon	${}^{12}\text{C}(d,p){}^{13}\text{C}$	p, γ
Nitrogen	${}^{14}\text{N}(d,p){}^{15}\text{N}$	p, γ
Oxygen	${}^{16}\text{O}(d,p){}^{17}\text{O}$	p, γ
Fluorine	${}^{19}\text{F}(p,\alpha){}^{16}\text{O}$	γ

Table 2

Energies of protons emitted at 135° from a number of elements when irradiated
with deuterons of 1.3 MeV

Reaction	Q(MeV)	Energy (MeV) of product nucleus level		E _{proton} MeV
$^{10}\text{B(d,p)}^{11}\text{B}$	9.237	0	(0)	8.866
	7.110	2.127	(1)	6.982
	4.778	4.459	(2)	4.926
	4.202	5.035	(3)	4.421
$^{11}\text{B(d,p)}^{12}\text{B}$	1.138	0	(0)	1.811
	0.191	0.947	(1)	0.998
	-0.536	1.674	(2)	0.393
$^{12}\text{C(d,p)}^{13}\text{C}$	2.722	0	(0)	3.250
$^{14}\text{N(d,p)}^{15}\text{N}$	8.615	0	(0)	8.704
	3.339	5.276	(1)	3.900
	3.310	5.305	(2)	3.874
	2.287	6.328	(3)	2.951
$^{16}\text{O(d,p)}^{17}\text{O}$	1.918	0	(0)	2.683
	1.047	0.871	(1)	1.895

AERE - R 8514 Fig. 1
Profile of carbon in a steel obtained by a discontinuous line scan

AERE - R 8514 Fig. 2
Distribution of carbon count in a steel
sample

AERE - R 8514 Fig. 3
Nitrogen profile obtained for a steel sample

A

B

C

AERE - R 8514 Fig. 4
Distribution of iron (A), carbon (B) and nitrogen (C) counts in a steel sample

AERE - R 8514 Fig. 5
A comparison of repeat scans with the nuclear microprobe

A

B

C

D

AERE - R 8514 Fig. 6
Recorded distribution of iron (A), chromium (B), carbon (C) and oxygen (D) counts from section
of tube with internal surface exposed to proton detector

A

B

C

D

AERE - R 8514 Fig. 7

Iron (A), chromium (B), carbon (C) and oxygen (D) counts obtained from section of a steel tube with internal surface not exposed to particle detector

A

B

C

D

AERE - R 8514 Fig. 8
Distribution of iron (A), carbon (B), oxygen (C) and boron (D) counts from a weld

AERE - R 8514 Fig. 9
Boron autoradiograph of weld