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QUANTITATIVE ELECTRON PROBE MICROANALYSIS
USING A SCANNING ELECTRON MICROSCOPE
AND AN X-RAY ENERGY SPECTROMETER

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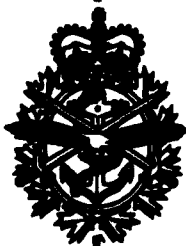### DARTMOUTH N.S.

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QUANTITATIVE ELECTRON PROBE MICROANALYSIS USING A SCANNING ELECTRON MICROSCOPE AND AN X-RAY ENERGY SPECTROMETER.

Dwight E. Veinot

April 1980

Approved by J. R. BROWN   A/Director / Technology Division

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ABSTRACT

A procedure was developed to utilize a scanning electron microscope and X-ray energy spectrometer to obtain quantitative elemental analysis. The precision and accuracy of an X-ray intensity ratio data processing technique has been evaluated. In general, the quantitative results obtained were accurate to better than ± 1 percent of the certified elemental compositions of standard reference materials for all elements present at greater than 2 weight percent. Results were reproducible to better than 1 percent of the determined percentage compositions. Elements present at less than 0.1 weight percent composition and elements having atomic numbers less than 11 (sodium) were not detected.

SOMMAIRE

On a mis au point un procédé qui utilise un micro-
scope électronique à balayage et un spectromètre d'énergie de
rayons-X afin de procéder à l'analyse quantitative des éléments.
On a procédé à l'évaluation de la précision ainsi que de la
fiabilité d'une technique de traitement numérique des rapports
d'intensité des rayons-X. De façon générale, les résultats
quantitatifs obtenus avaient une précision supérieure à ± 1
pourcent des compositions bien connues en éléments présents
dans des matières de référence étalons pour le cas de tous les
éléments présents dans une proportion supérieure à 2 pourcent
en poids. Les résultats pouvaient être reproduits dans une
proportion qui dépassait 1 pourcent des compositions déterminées
en pourcentage. Les éléments dont la présence représentait
moins de 0.1 pourcent en poids de la composition et les éléments
dont les numéros atomiques étaient inférieurs à 11 (sodium)
n'ont pas été décelés.

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NOTATION

SEM	scanning electron microscope
XES	X-ray energy spectrometer
FWHM	full width half maximum
eV	electron volt
KV	kilovolt
ac	alternating current
A°	Angstrom
mm	millimeter
μm	micrometer
cps	counts per second
ADC	analog to digital converter
PGT	Princeton Gamma Tech
NBS	National Bureau of Standards
SRM	Standard Reference Material

1. INTRODUCTION

The use of X-rays to obtain chemical analysis has expanded since the relationship between X-ray line frequency and atomic number was first discovered[1]. One of the most recent advances in this area was the development of solid state, energy dispersive radiation detectors. Such devices can be fitted conveniently to scanning electron microscopes and can accurately resolve the energies of X-rays produced by electron bombardment of the sample (target) material in the SEM.

The high energy resolution capability of lithium drifted silicon radiation detectors has resulted in considerable interest in their potential use as analytical devices[2]. The most interesting feature of these devices is their capability to rapidly and simultaneously detect and discriminate X-ray energies. Energy dispersive spectrometers have been used in combination with electron microprobes and electron microscopes to simultaneously obtain chemical and topographical information on samples such as metals, plastic, glass, rubber, solvent residues, ceramics, semi-conductors, paints, airborne particulates and corrosion products. Several reports[3,4,5,6,7,8,9] have been published describing the analytical applications of electron probe microanalysis. Some of these[4,5,7,9] contain information concerning accuracy, precision and detections limits obtained using energy dispersive spectrometers for chemical analysis.

The aim of this work was to develop and evaluate a procedure to utilize a SEM-XES combination to obtain rapid and reliable chemical analyses during a microscopic examination. This procedure enables an analyst to obtain chemical information from very small samples (less than 1 μm^2) and also to isolate and analyze specific areas of interest on the surfaces of larger samples.

2. EQUIPMENT

An Advanced Metals Research (AMR) model 1000A SEM which incorporates a pre-aligned electron optical column, a secondary electron detector and a specimen stage assembly which enables specimen rotation, tilt and x, y, and z translation was used for this work. The display console contains

a cathode ray tube display screen together with electron optics controls such as magnification, working distance, brightness, contrast, accelerating voltage, filament current and beam alignment.

A Princeton Gamma Tech (PGT) lithium "drifted" silicon X-ray detector model 1S-15 complete with associated PGT model PO-12 preamplifier, model 340 main amplifier, model 343 live time corrector and a 7.5 litre liquid nitrogen dewar formed the basis of the X-ray detector system. The detector bias voltage (-1000V dc) was provided by a Tennelec model TC 947 supply. The detector resolution was 148 eV FWHM at 5.9 keV and 1000 cps.

A Tracor Northern NS 880 X-ray analysis system consisting of a magnetic cassette tape transport, an NS 623 analog to digital converter (ADC) having 8192 channels and a PDP 11/05 computer with 20 K of core memory was used to acquire and process the X-ray data. Software used with this system was developed by Tracor Northern.

An Edwards model 306 vacuum coater was used to deposit a thin conducting carbon film on the surfaces of specimens in order to reduce charge build-up caused by electron bombardment inside the SEM.

A Keithley model 602 electrometer was used in conjunction with a device prepared in the laboratory to measure electron beam currents.

An Invertron model LC-1201B dynamic AC line corrector provided a stabilized voltage from 110V ac mains.

3. EXPERIMENTAL PROCEDURES

3.1 Approach

An X-ray intensity ratio technique formed the basis for the quantitative analytical procedure which was developed. Elemental X-ray intensities from the sample being analyzed were compared to the corresponding pure element X-ray intensities. Selected standard reference materials (NBS) were used to evaluate the accuracy and precision of the technique.

3.2 System Calibration

The front end electronics of the X-ray analysis system were calibrated using X-rays released from a pure moly-

bdenum specimen. The molybdenum Lα X-ray (2293 ev) and Kα X-ray (17478 eV) provided a convenient means of adjusting energy calibration over a wide energy range (15185 eV).

3.3 Sample Preparation

All samples were mounted in epoxy resin and polished to a flat smooth surface using standard metallographic techniques. The polished specimens were cleaned in methanol to remove excess polishing compound and dried in air. A thin (100 A°) conductive carbon layer was deposited on the specimen surfaces in order to prevent charge build-up on the non-conducting epoxy mounts during the analyses.

A graphite rod (spectrographic grade) was machined to 1 mm diameter (EFFA Sharpener, Ernest F. Fullam, Inc., N.Y.) and set to provide a 5 mm burn in the Edwards vacuum coater in order to reproduce carbon coatings of the same thickness. Carbon was used for the coating material because it is conductive, does not appreciably affect the electron beam bombardment or X-ray emission and does not itself produce X-rays which are detected by the system.

3.4 Electron Beam Parameters

The rate of production of X-rays from the sample surface is directly proportional to the rate of electron bombardment upon the specimen surface (beam current). Therefore, in order to obtain a material balance in chemical analyses it was necessary to measure and control beam current during the acquisition of pure element reference spectra and during subsequent analyses of samples of unknown composition using these references. A means of measuring beam current at the sample surface was not available for the AMR model 1000A SEM so a device (Figure 1) was prepared in the laboratory and fitted to the SEM stage assembly as follows. A 1 mm i.d., 4 mm deep cylindrical hole was drilled into a solid piece of aluminum. This hole was covered with a metallic foil having a 500 μm i.d. aperature to allow electron beam entrance to the drilled cavity. Electrically conducting silver paint (Number 1481 silver paint E.F. Fullam, N.Y.) was used to assemble this device and secure it to a standard aluminum specimen stub so that it could be conveniently fitted to the specimen stage assembly. The stage assembly was connected to an electrical contact leading to the outside of the electron optical column using insulated copper wire. A Keithley model 602 electrometer was connected to this outside contact using a short length (20 cm) of shielded coaxial cable.

The carbon coated specimens (pure element standards and NBS certified standard reference materials) and the alu-

minum cage were positioned on the stage assembly using a multiple
sample holder similar to that described by Green[10]. The use of
this holder enables the analysis of several samples without re-
quiring separate introduction of these samples into the sample
chamber. This is particularly useful when using the SEM-XES
combination to analyze several samples because it allows each
specimen to be analyzed without having to re-establish electron
beam or column conditions between the analyses.

The electron beam was focused onto the specimen sur-
face. The Z-translational adjustment was used to provide a
working distance* of 12 mm which was held constant for each
analysis. The tilt adjustment was used to provide a take-off
angle** of 35 degrees from each sample surface. The electron
beam was then focused into the hole in the aluminum cage. The
resulting current was measured with the Keithley electrometer.
Typical currents produced were of the order of 10^{-9} amperes.
A current of 0.5×10^{-9} amperes was selected for the quanti-
tative procedure because it was easily obtained and remained
steady for long periods of time (hours). The beam current was
adjusted and controlled as required using the filament current
and beam alignment controls on the SEM. Current measurements
were made before and after each analysis. Typically these
measurements did not vary by more than $\pm$ 4 percent.

3.5 Data Acquisition and Processing

Using an accelerating voltage of 30 kV, the X-ray
energy spectrum of each of the pure element standards was ob-
tained and stored on magnetic tape. The X-ray energy spectrum
of each of the NBS certified standard reference materials used
to evaluate the technique was obtained in a similar manner.

X-ray intensity ratios (k_i) were converted to ele-
mental concentration ratios (c_i) using the Tracor Northern
Super ML[11] and ZAF[12] computer programmes which were designed
to process the basic expression:

$$c_i = k_i (ZAF)_i$$

 * Distance from column anode to sample surface.

** Angle formed by the sample surface and the path of X-rays
    to the detector at the point of electron beam penetration.

where Z is an atomic number penetration correction factor and A and F are computed absorption and fluorescence correction factors for element i. Since each of the three correction terms requires a knowledge of the concentrations for all elements in the sample, it is necessary to solve the ZAF corrections in an iterative manner similar to that used by J. Colby in the Magic IV programme[13]. In that programme the estimated concentrations are set equal to the input k ratios and the concentrations are then normalized to sum to 100 percent. Using the normalized c_i values, the ZAF factors for each element are computed from expressions developed by Duncumb and Reed[14].

4. RESULTS AND DISCUSSION

Tables 1, 2, and 3 show the results obtained for the analyses of three different alloys. Table 1 shows the results obtained for NBS SRM 162a monel alloy. Table 2 shows the results obtained for NBS SRM 134 high speed steel alloy. Table 3 shows the results obtained for NBS SRM 62d manganese bronze alloy. All results were obtained using the same set of pure element reference spectra. Typically, percentage errors in the analyses were less than 1 percent for elements present at greater than 2 weight percent in the sample. However, an error of 3.48 percent was obtained for the analysis of chromium present at 3.60 weight percent in NBS SRM 134 (Table 2) and an error of 1.10 percent was obtained for copper present at 59.67 weight percent in NBS SRM 62D (Table 3). In general, the accuracy of the analyses deteriorated as concentrations decreased below 2 weight percent and elements present at less than 0.1 weight percent were not detected. These results compare favourably with those obtained by Desborough and Heidel[5] who used electron beam excitation and a more complicated system consisting of several single channel analyzers to obtain quantitative analytical results.

The precision of the analytical results obtained using this technique was expressed by a calculation of the range (difference between highest and lowest) of the determined elemental weight percentages of three separate analyses of the same area on each of the three alloys. As shown in Tables 1, 2, and 3 the range was never greater than one weight percent for any of the elements determined. In general, the precision of the analyses was found to decrease as elemental concentrations increased. That is, the range of a set of analyses was larger for elements present at higher weight percent compositions. This finding was evident in all of the alloys analyzed and is due to the fact that the standard deviation of a given number of collected x-ray counts varies as the square root of the number of counts.

The analysis volume (volume from which X-rays were emitted) was calculated to be of the order of 10^{-4} μm^3 using an average X-ray escape depth of 1 μm and a minimum beam diameter of 1×10^{-2} μm. This capability of the SEM-XES system to provide a quantitative "point" chemical analysis of such small sample volumes has many useful applications. For instance, the SEM-XES combination has been used to analyze small particulate wear debris collected from lubricating oils by filtration or ferrography. Also, a "point" analysis can provide elemental concentration profiles across a diffusion boundary which can be used to calculate the diffusion coefficient of one element into the sample matrix.

The technique used to obtain material balance in the chemical analysis provided added certainty in the analyses since the total of the determined elements in each sample was at least 97 percent. An immediate advantage of this capability is that a single element for which no reference spectrum is available can be calculated by difference. For example, if an alloy is found to contain an element from the qualitative analysis but no reference spectrum is available then a reasonable estimate of the concentration of that element can be obtained by doing a material balanced quantitative analysis and subtracting the total determined concentrations from 100 percent. This procedure can only be used to determine one additional element in each sample and the analyst must be certain that that element is present in the sample.

5. SUMMARY

A procedure was developed to obtain quantitative elemental analysis of flat polished metallic specimens using a scanning electron microscope and X-ray energy spectrometer. The technique enables the acquistion of chemical information from micro quantities of sample or from small areas of interest in the matrix of larger samples. Accurate and reproducible quantitative results were obtained on areas of the order of 10^{-6} μm^2. The technique is considered a surface analysis technique because only X-rays from approximately 1 μm deep in the sample are detected. An accuracy of $\pm$ 1 percent was typical for the determination of elements present at greater than 2 weight percent. A sensitivity of approximately 0.1 weight percent was found for most elements.

ACKNOWLEDGEMENT

TABLE 1

MONEL TYPE ALLOY - NBS SRM 162a

Element	Determined Composition Weight %	Range Weight %	NBS Certified Composition Weight %	Error Percent
Ni	64.10	0.96	63.95	0.23
Cu	30.42	0.53	30.61	0.62
Fe	2.17	0.15	2.19	0.91
Mn	1.48	0.08	1.60	7.50
Si	0.97	0.10	0.93	4.30
Al	0.45	0.08	0.50	10.00
Cr	N.D.	--	0.042	--
Co	N.D.	--	0.076	--
Ti	N.D.	--	0.005	--
Ca	N.D.	--	0.013	--
S	N.D.	--	0.007	--
C	N.D.	--	0.079	--
TOTAL	99.59			

Note: N.D. = Not Detected

TABLE 2

High Speed Steel Alloy - NBS SRM 134

Element	Determined Composition Weight %	Range Weight %	NBS Certified Composition Weight %	Error Percent
Fe	82.04	0.50	82.01	0.04
Cr	3.60	0.38	3.73	3.48
Mo	8.70	0.50	8.68	0.23
W	1.71	0.42	1.82	6.04
V	1.19	0.11	1.13	5.30
Mn	0.22	0.06	0.155	29.55
Si	0.29	0.10	0.323	10.22
Ni	N.D.	--	0.077	--
S	N.D.	--	0.006	--
P	N.D.	--	0.016	--
C	N.D.	--	0.810	--

TOTAL   97.75

Note: N.D. = Not Detected

TABLE 3

Manganese Bronze Alloy - NBS SRM 62d

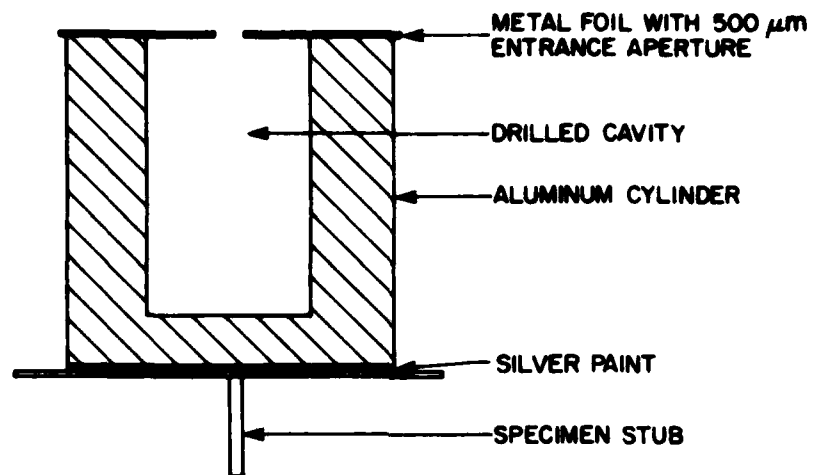| Element	Determined Composition Weight %	Range Weight %	NBS Certified Composition Weight %	Error Percent
Cu	59.67	0.97	59.02	1.10
Zn	37.07	0.97	37.14	0.19
Al	1.19	0.08	1.23	3.25
Mn	0.57	0.10	0.66	13.64
Sn	0.36	0.08	0.38	5.26
Fe	0.88	0.08	0.89	1.12
Ni	0.23	0.04	0.28	17.86
Pb	N.D.	--	0.23	--
Si	N.D.	--	0.075	--
TOTAL	99.97			

Note: N.D. = Not Detected

FIG. 1: Cross-section of Electron Capturing Device

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DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall document is classified)

1. ORIGINATING ACTIVITY	2a. DOCUMENT SECURITY CLASSIFICATION
Defence Research Establishment Atlantic, Dockyard Laboratory, FMO Halifax, N.S. B3K 2X0	Unclassified
	2b. GROUP

3. DOCUMENT TITLE

Quantitative Electron Probe Microanalysis Using a Scanning Electron Microscope and an X-ray Energy Spectrometer

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)   Tech Memo

5. AUTHOR(S) (Last name, first name, middle initial)

Veinot, Dwight E.

6. DOCUMENT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
April 1980	20	14

8a. PROJECT OR GRANT NO.	9a. ORIGINATOR'S DOCUMENT NUMBER(S)
	DREA TECHNICAL MEMORANDUM 80/A
8b. CONTRACT NO.	9b. OTHER DOCUMENT NO.(S) (Any other numbers that may be assigned this document)

10. DISTRIBUTION STATEMENT

11. SUPPLEMENTARY NOTES	12. SPONSORING ACTIVITY
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KEY WORDS
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