QUANTITATIVE LIGHT ELEMENT ANALYSIS USING EDS

D. Bloomfield, G. Love, V. Scott

► To cite this version:

D. Bloomfield, G. Love, V. Scott. QUANTITATIVE LIGHT ELEMENT ANALYSIS USING EDS. Journal de Physique Colloques, 1984, 45 (C2), pp.C2-181-C2-184. 10.1051/jphyscol:1984241 . jpa-00223954

HAL Id: jpa-00223954

<https://hal.science/jpa-00223954>

Submitted on 1 Jan 1984

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

QUANTITATIVE LIGHT ELEMENT ANALYSIS USING EDS

D.J. Bloomfield, G. Love and V.D. Scott

School of Materials Science, University of Bath, U.K.

Résumé - La méthode décrite traite du bruit de fond et des superpositions de pics dans les spectres en énergie des éléments très légers, ce qui permet de réaliser une analyse quantitative et d'améliorer la sensibilité de la détection des éléments légers.

Abstract - A method is described for dealing with background and peak overlap in light element ED spectra which enables quantitative analysis to be carried out and also improves light element detection sensitivities.

1. INTRODUCTION

When energy-dispersive (ED) spectrometers are used for quantitative electron-probe microanalysis it is necessary to process the ED spectra before reliable x-ray intensity measurements can be achieved. Processing involves subtracting the background to provide an accurate measure of the peak intensity and also dealing with any overlap from neighbouring x-ray lines. Although methods exist for analysing elements of atomic number above eleven, see for example (1,2), it is by no means certain they are suitable for lighter elements.

We have been investigating the prospects of carrying out quantitative light element analysis using an EDAX ECON detector coupled with a 711 analyser. In addition to comparing quantitative ED results with corresponding wavelength-dispersive (WD) data, some comments are made concerning ED detection sensitivities for carbon, nitrogen and oxygen.

2. QUANTITATIVE ANALYSIS

Here we shall assess new methods for dealing with background removal and overlapping peaks in soft x-ray ED spectra.

The new technique of background subtraction takes into account an artefact, or 'spur', discovered in the background as well as the noise counts (3), and then deals with the residual x-ray continuum (4) using a method developed by Smith et al (5) which itself is based upon Kramer's Law. This method is then compared with that based upon linear interpolation of the x-ray background beneath the x-ray peak. The latter can be applied only if there are no problems of peak overlap and, has been used merely as a basis for comparison. Assessment of both techniques is carried out using a series of specimens and standards and then comparing the respective nett peak intensity ratios with similar data obtained from WD measurements where the problem of background subtraction is trivial.

In order to deal with the peak overlap problem those peaks which contribute to the overlap are recorded from pure element standards and backgrounds are then removed. These spectra are then added together and their respective intensities adjusted so that when superimposed on the calculated background for the specimen the resultant profile matches that of the overlapped peak. Correspondence is achieved using least squares analysis (4).

All specimens and standards were given a fine polish and non-conducting materials were coated with a thin ($\sim 10\text{nm}$) layer of gold; (in these cases the corresponding standard was similarly coated). X-ray measurements were carried out using a JEOL JXA-50A microanalyser fitted with a cold finger which was operated throughout the analysis to minimise contamination. The take-off angle for both ED and WD spectrometers was 35° so the x-ray data obtained were directly comparable.

TABLE 1. Intensity Ratios. Fluorine, oxygen and carbon standards are MgF_2 , Al_2O_3 and graphite respectively.

X-ray line	Specimen	WD		ED			
		7kV	15kV	Linear Interpolation		New Method	
		7kV	15kV	7kV	15kV	7kV	15kV
F_k	PbF_2	0.196	0.105	0.205	0.109	0.208	0.110
O_k	NiO	0.444	0.458	0.485	0.483	0.454	0.463
C_k	SiC	0.0951	0.0374	0.0766	0.0188	0.0933	0.0366
C_k	Fe_3C	0.0497	0.0191	0.0286	0.0080	0.0504	0.0198

Table 1 lists the first series of specimens and standards used, together with the x-ray line being measured; these samples were selected such that no overlap problems arose. Figure 1 shows the low energy end of the ED spectrum from Si_3N_4 , in which the nitrogen K peak is clearly resolved from the noise counts at $\leq 140\text{eV}$. Linear interpolation of the background is shown by the dotted line and counts below the line were subtracted from the total counts under the peak to give the nett nitrogen peak intensity. This procedure was carried out at 7 and 15 keV for the specimens and standards listed in Table 1 and the data presented as x-ray intensity ratios ($k = I_{\text{spec}}/I_{\text{std}}$) also in Table 1. Corresponding k ratios are included for the WD results, and here it was necessary to integrate the peaks in order to minimise the effects of chemical bonding on peak shape (6). It may be seen that whilst agreement between the ED and WD data is reasonable for fluorine, it becomes progressively worse with decrease in atomic number, irrespective of whether a probe voltage of 7 or 15keV was used. The result of applying our new method of background subtraction to the Si_3N_4 spectrum is shown by the unbroken line in figure 1. It is clear that the nett nitrogen peak intensity given is appreciably higher than with linear interpolation. Data obtained from all systems are included in Table 1. It may be seen that close correspondence of k values is achieved with the respective WD data, from which it may be concluded that our technique gives satisfactory representation of the background under the peak and allows sensible quantitative ED data to be obtained in light element work.

A second series of samples listed in Table 2 are all likely to present some overlap in the soft x-ray region of the spectra. An ED spectrum is illustrated in figure 2a, the dotted line showing the background calculated using our method (note the small discontinuities associated with the K absorption edge for oxygen and the L absorption edge for iron). In figure 2b are shown the deconvoluted peaks for titanium L, oxygen K and iron L lines after background subtraction. A similar pair of diagrams is shown for MnF_2 in figures 3a and 3b. In this example the respective x-ray energies are 677eV (fluorine K) and 637eV (manganese L) i.e. the peaks are only separated by 40eV. Similar results were obtained for the other systems studied.

Using the standards listed in Table 2 x-ray intensity ratios (k) were obtained and these are also given in the table (after application of our background and overlap corrections). Included as well are corresponding k values obtained using WD methods; not only was there no background subtraction problem with these

measurements, but also the good spectral resolution of the system meant that all x-ray lines were clearly resolved. The ED results differ by only a few percent from the WD values which indicates that our method for dealing with overlapping peaks in the soft x-ray region works very satisfactorily.

TABLE 2. Intensity Ratios

X-ray line	Standard	Specimen	WD		ED-New Method	
			7kV	15kV	7kV	15kV
F _k	MgF ₂	MnF ₂	0.339	0.144	0.363	0.148
O _k	Al ₂ O ₃	Fe ₂ TiO ₅	0.593	0.472	0.589	0.460
O _k	Al ₂ O ₃	MgCr ₂ O ₄	0.826	1.060	0.837	1.100
N _k	Si ₃ N ₄	Nitrided steel	0.258	0.451	0.252	0.284

3. DETECTION SENSITIVITY

Detection sensitivities for the elements carbon, nitrogen and oxygen were determined using samples of SiC, Si₃N₄ and Al₂O₃ respectively. The total counts under the peak ($\pm 70\text{eV}$ either side of the maximum) were recorded. The background (B) was then calculated for this channel width and the nett peak counts (P) determined. The sensitivities were calculated according to

$$3C_A (B/P^2)^{\frac{1}{2}}$$

where C_A is the concentration of the light element in the specimen. Measurements were carried out using a specimen current of 0.5nA for 200 seconds ('real' time) at several different kilovoltages. Results for the three systems are illustrated in figure 4. The data show that there is an optimum voltage for each element in these specimens. The minimum in the curve arises because there is an increase in the intensity of generated x-rays with kV but this is counteracted by an increase in absorption as the x-rays are excited at greater depths in the target. The optimum detection sensitivities were: for carbon in SiC, 0.3wt% at 5kV; for nitrogen in Si₃N₄, 0.5wt% at 7kV; for oxygen in Al₂O₃, 0.12wt% at 11kV. Statistics would lead one to believe that these figures could be improved by using longer counting times but then other problems may arise to instability in the equipment and contamination of the specimen. Nevertheless they serve as a useful guide to what may be achieved. Certainly they are much better than previously published data in which little or no attempt had been made to deal properly with background subtraction. The values will depend upon the system being analysed. For example, carbon sensitivity figures in Fe₃C tend to be lower ($\sim 0.18\text{wt}\%$) than in SiC because, although the background level is higher in this material, absorption of carbon radiation is less than in SiC. Clearly, then, each system has to be considered separately when quoting detection sensitivities and any overlap problems undoubtedly will adversely affect the values.

4. CONCLUSIONS

A method of background subtraction has been developed which can deal properly with light element ED spectra. It is also shown that problems due to peak overlap in this region of the spectrum may be satisfactorily solved. Application of these techniques enables quantitative light element analysis to be achieved from ED spectra, and also improves light element detection sensitivities.

Acknowledgements

To MOD and SERC for support.

REFERENCES

1. RUSS, J.C., X-ray Spectrom. 6 (1977) 37.
2. STATHAM, P.J., J.Microsc. 123 (1981) 1.
3. BLOOMFIELD, D.J., LOVE, G., SCOTT, V.D., X-ray Spectrom. To be published.
4. BLOOMFIELD, D.J., and LOVE, G., X-ray Spectrom. To be published.
5. SMITH, D.G.W., GOLD, C.M. and TOMLINSON, D.A., X-ray Spectrom 4 (1975) 149.
6. LOVE, G., COX, M.G.C. and SCOTT, V.D. J.Phys.D: Appl.Phys. 7 (1974) 2131.

Fig.1. Nitrogen peak from Si_3N_4 ; background calculated using new method — linear interpolation ---.

Fig.2. Spectrum from Fe_2TiO_5
(a) Original spectrum with background level superimposed - note steps from absorption edges
(b) deconvoluted spectrum.

Fig.3. as for Fig.2. but spectrum of MnF_2

Fig.4. detection sensitivities versus kV
+ carbon in SiC
x nitrogen in Si_3N_4
* oxygen in Al_2O_3