ACCURACY, REPRODUCIBILITY AND SCOPE FOR X-RAY MICROANALYSIS WITH Si(Li) DETECTORS

P.J. Statham

Link Systems Ltd, Halifax Road, High Wycombe, Bucks HP12 3SE, U.K.

Résumé— On discute de l'état actuel de la microanalyse par rayons X, plus particulièrement de la précision et des limites de détection, des corrections dues aux superpositions de pics et de l'utilisation des détecteurs sans fenêtres.

Abstract— The current state of the art for x-ray microanalysis is discussed with particular reference to accuracy and limits of detection, corrections for peak overlap and use of "windowless" detectors .

It is now about ten years since reports appeared in the literature claiming that Si(Li) spectrometers (EDS) could be used for routine electron microprobe x-ray analysis giving results with accuracy comparable to those achieved using Bragg crystal spectrometers (WDS). EDS analysis is now an established technique for use with transmission electron microscopes where the x-ray yield is particularly low and although electron energy loss spectrometry (EELS) is finding increasing popularity, there is still no satisfactory alternative for general microanalysis of chemical composition. A recent review /1/ covers most aspects of the use of EDS in microanalysis and a later paper /2/ discusses prospects for improvement in this field. This paper will present specific examples to demonstrate results which are attainable with "state-of-the-art" equipment and show where WDS takes over as the more appropriate technique.

1. Spectrum processing

The two dominant techniques for spectrum processing, namely background modelling with a function based on physical theory and digital filtering with least-squares peak fitting (FLS) have been discussed at length /1/. However, theoretical arguments for the validity of a given technique are no substitute for experimental evidence of its success in real applications. To this end it is important to test the overall EDS system. A simple, yet demanding, series of tests can be built around analyses of a known pure sample; if the EDS system is programmed to assay elements which are known not to exist in the sample, the results for these elements (which should be zero) give an indication of the reliability of spectrum processing /3,4/. Figure 1 shows the results of some tests on a specimen of pure silica. Spectra were analysed using a Link 860 EDS system using the ZAF4/FLS program which employs the filtering/ least-squares fitting technique and gives an estimate of statistical error which is valid provided there is no instrumental drift or sample-related systematic error. As shown in fig.1, the means for both Al and P show no significant bias, the minimum and maximum results fall within ± 3 standard deviations of the true value and the standard deviation estimated by calculation from the results is close to the value predicted by the FLS program which includes contributions associated with background and peak overlap /5/. In this example , it is important to have verified that spurious concentrations of elements are not detected at the 3-sigma confidence level.

Fig.1:

Results from tests on pure silica specimen, 100 secs per analysis. Plot shows position of Al and P peaks relative to Si and data is summarised to show correct determination of Al and P areas by FLS routine to within degree of statistical uncertainty.

EDS analysis of PbS using ZAF4/FLS:

Fig.2: Analysis of PbS sample by ZAF4/FLS program. For each spectrum, total count rate was about 3kHz and time was 100 secs.

While this type of "null" test is very useful, it is still necessary to verify that spectrum processing produces the correct peak areas even under conditions of severe overlap. Figure 2 demonstrates a particularly difficult case where the Pb M lines interfere strongly with the S K lines. The results of 10 analyses of a lead sulphide specimen are shown to demonstrate that not only is deconvolution possible, but the results are reproducible and show fluctuations which are consistent with the expected statistical variation as predicted by the ZAF4/FLS program. It is also worth noting that the relative statistical accuracy for Pb is about 1% and for S is around 2% for these typical analyses with 100 seconds acquisition time and 3 kHz total spectrum count rate. In general, for such rates and acquisition times, accuracy for elemental concentrations greater than 10 % should be comparable to that expected for ZAF x-ray correction procedures and this is substantiated by other investigators /e.g. 6,7/.

2. Analysis of light elements

Analysis with EDS has traditionally been limited to elements sodium and above in the periodic table. This limitation stems from use of a beryllium window to isolate the vacuum within the Si(Li) detector enclosure from the outside air. For some years now, detectors have been produced where the Be window can be removed once the detector is in a clean vacuum environment within a microscope specimen chamber. The performance of such "windowless" detectors at very low photon energies is limited primarily by electronic noise and it has been shown that if noise can be reduced sufficiently by use of special FETs and pulse-processing electronics, then even Boron can be detected /2/. In our detector laboratory, we occasionally see exceptional performance from a detector and figure 3 shows a spectrum from a beryllium foil showing a small but unmistakable Be peak (which did not appear when the sample was removed!). Although this result is encouraging, it would be unfair to suggest that EDS is now capable of Be analysis in practice because even in this case, the 3-sigma detection limit is of the order of 25 % and the majority of detectors cannot match this performance. If quantitative analysis is required for light elements, there are severe problems to be solved associated with specimen preparation to produce a flat surface, coating to reduce specimen charging and calculation of a realistic specimen-absorption correction which are discussed elsewhere /8/.

Fig.3: Detection of Be from Be foil in SEM using Link LZ5 detector

3. Detection limits

The case is frequently made that it is very difficult to define detection limits because they depend on so many factors. Though this is correct, it is also unsatisfactory to dismiss the topic because some guidelines have to be established to define when the technique should and should not be applied. Figure 4 shows a graph of detection limits attainable for EDS with and without a Be detector window and this must be qualified carefully before the results are used. A detection limit value must always be calculated with reference to the exact spectrum processing technique that will be used to establish the presence or absence of a peak /9/ so fig.4 shows a formula which assumes a very simple background subtraction making use of windows either side of the peak window. Since count rate, beam current and counting time are all significant, these results pertain to a configuration which gives about 100,000 counts in the Co peak when a pure Co specimen is used. Though the boron result has been demonstrated previously /2/ and the beryllium value has only recently been obtained, these are not typical but most windowless detectors should give equivalent performance for elements carbon and beyond. Peak overlap will result in higher values and sample matrix has an effect but the general conclusion is that for the majority of elements of common interest, detection limits are around 0.1 weight %. The term "detection limit" is somewhat misleading /9/ but may be used to indicate a level of concentration where the EDS technique gives a completely unreliable result.

Fig.4:

A general guide to 3-sigma detection limits attainable with EDS. Background regions with integrals B1 and B2 have widths equal to half the width of the peak window with net integral P' counts. C is the concentration for the element used in the test sample. The results may be expected for conditions which would result in 100,000 counts being accumulated in the Co K peak for a pure cobalt specimen.

4. Rough surfaces and particles

An EDS system accumulates data from all x-ray energies simultaneously and as the detector is non-focussing, spectra can be acquired from both rough surfaces and particles. In order to minimise the errors resulting from imprecise specimen geometry, sample size and shape, the "peak-to-background" (P/B) method was introduced for such samples. The technique has been put into context with other methods for particle analysis by Small /10/ and spectrum processing methods and applications to analysis of rough surfaces have been discussed by this author /11/. Figure 5 shows some results obtained on glass particle samples obtained from the National Bureau of Standards and analysed with a 20 kV beam using the Link ZAF/PB program which employs published spectrum processing and calculation procedures /11,12/. As the K1727 results show, the P/B technique may give results which, for larger particles, can be achieved by simply normalising the results of conventional ZAF analysis. However, in terms of absolute results, ZAF/PB gives totals and results which spread over a much narrower range than with standard analysis. The K411 result exemplifies the performance on small particles where the mass effect gives a low total for conventional ZAF. Whereas the the ZAF/PB results are generally better, the Fe value is distinctly high and refinements may be required to the P/B method to handle very small particles /10/.

ANALYSES OF NBS K411 GLASS PARTICLES

1.5-3µm diameter, average of 7 analyses
(oxygen calculated by stoichiometry):

Nominal %	ZAF	ZAF/PB
Mg 8.9	7.3	8.2
Si 25.7	24.2	25.4
Ca 11.2	10.3	11.9
Fe 10.2	12.0	11.8
min. total:	72 %	97 %
max. total:	103 %	104 %
avg. total:	93 %	102 %

ANALYSIS OF NBS K411 GLASS PARTICLE

2µm diameter particle:

Nominal %	ZAF	ZAF/PB
Mg 8.9	5.8	7.9
Si 25.7	18.7	24.9
Ca 11.2	7.8	12.7
Fe 10.2	9.3	12.0
Total(+O):	71.9	101.3

Fig.5: Results of analyses of NBS glass particles supported by formvar film on 200 mesh Cu grid using 20kV SEM

5. Analysis of thin foils

Although quantitative analysis is now well-established for polished bulk samples, a certain amount of controversy surrounds the analysis of thin specimens. Although correction procedures are considerably simplified for a thin foil, accurate compositional analysis demands knowledge of the sensitivity factor for each element. There are many compilations of theoretical "k-factors" in the literature but to this author's knowledge, table 1 summarises results from the only three comprehensive sets of experimental data that have been published for 100 kV microscopes. Whereas the differences for Na, Mg, Al, Mo and Ag could be due to detector efficiency variations, there is no obvious explanation for discrepancies for Cr and Ni when results for Ti, Fe and Cu are closely comparable. If experimental errors and as-yet undetermined instrumental effects are responsible, then one must take the view that worst-case errors of up to 25% could be expected in standardless analysis; otherwise much more experimental verification is required before a universally-applicable set of k-factors can be established.

Table 1: kXSi factors for microanalysis of thin foils in transmission microscopes. Experimental data in this table were reviewed by Wood *et al* /13/ and the values are reproduced here for convenience. Values are not reproduced if no comparison could be made between two investigator's results.

	Wood <i>et al</i> 120 kV	Cliff/Lorimer 100kV (1)	(2)
Na	3.57	5.77	3.2
Mg	1.49	2.07	1.6
Al	1.12	1.42	1.2
Si	1.00	1.00	1.00
K	1.12	-	1.03
Ca	1.15	1.00	1.06
Ti	1.12	1.08	1.12
Cr	1.46	1.17	1.18
Mn	1.34	1.22	1.24
Fe	1.30	1.27	1.3
Ni	1.67	1.47	1.48
Cu	1.59	1.58	1.60
Mo	4.95	4.3	-
Ag	12.4	8.49	-

6. Combined EDS/WDS

With the additional of suitable control hardware, the operations of a crystal spectrometer and mechanical stage can be automated and the results of WDS and EDS analysis combined. A practical demonstration of the advantages appears in the analysis of "Rhum" olivine: the trace elements Mn and Ni are best analysed by WDS whereas the major elements Mg, Si and Fe would require crystal changes between TAP, PET and LIF so EDS is more convenient. An experiment was performed using a Link SPECTA package which integrates output from a Cameca CAMEBAX spectrometer and EDS (T.Hopkins, pers.comm.) In the experiment, ten points were analysed for 200 seconds at each point. In the first run, only EDS was used but in the second run, counts for 100 seconds were taken by WDS on the Mn and Ni peaks whilst EDS acquisition was in progress. With EDS only, the results for Mg, Si and Fe were correct but Mn and Ni values were sometimes below the 3-sigma detection limit. With EDS and WDS, the average values for Mn and Ni, 0.23% and 0.37% were close to the expected values for these elements.

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