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PRACTICAL CONSIDERATIONS FOR EDS ANALYSIS IN AN AEM

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INTRODUCTION

EDS analysis of thin specimens in an analytical electron microscope is a powerful technique uniquely suited to a wide variety of analytical problems. It is a true "microanalytical" technique, even when compared to electron microprobe analysis, because AEM techniques easily permit the analysis of 10^{-4} to 10^{-6} the volumes analysed by EMPA techniques on bulk samples. However, under the conditions and constraints of operation of an AEM, additional analytical problems arise which are not in general encountered in EMPA work. These problems are often subtle, and prove hazardous to EDS analysis in the AEM. This paper will review the practical considerations attendant to the collection and interpretation of both qualitative and quantitative EDS data with which the analyst must be concerned before AEM results can be obtained which are as accurate as the technique theorectically permits. The theoretical aspects of EDS quantification schemes have been given in several excellent review articles (1,2,3), and will not be discussed here.

QUALITATIVE ANALYSIS

A. Sources of Spectral Artefacts and Composition Changes From Sample Preparation Effects

Specimens are typically prepared from bulk materials by a number of techniques, including ion-beam milling, electropolishing, chemical polishing, crushing to produce thin flakes, extraction replicas, ultramicrotomy, and others. Each technique can cause analysis difficulties (2,3), some by deposition of foreign elements onto the specimen surface, by selective removal of elements from phases in the specimen, by causing elements to migrate within the specimen, or by simply distorting the structure so that accurate determination of the location of elements in the specimen is difficult. Typical effects in ion-beam milling include: Ar ion implantation, deposition of Si (from silicone DP oil), deposition of elements (Fe, Ni, Cr, Ta) from gun and specimen holder materials, element migration by sample heating or ion bombardment effects, and possibly contamination of one specimen by elements from another specimen when a dual ion milling device is improperly used. Samples prepared by chemical or electropolishing techniques can have elements from polishing baths contaminate the surface, re-deposition of elements to form thin surface films, and selective removal of elements. Particles extracted from a matrix might have residual matrix elements remaining on the surface. Microtomy and crushing techniques can produce phase overlap problems which are not as easy to distinguish as phases in ion-milled foils. The clear caution is that when critical analyses are needed, data should be taken from samples prepared by more than one technique, whenever possible.

B. Systems Peaks

"Hole counts" are usually significant on older, unmodified instruments and may be significant even on more recent instruments. These system peaks should be reduced to an insignificant level so they need not be subtracted from the sample spectrum. Systems peaks generated after the beam strikes the specimen can result from BSEs, characteristic and continuum radiation which hits specimen chamber components (specimen grids, support washers, specimen holder, pole piece, cold trap, aperture blade, etc.). Modifications (4,5,6) should be made so that no detectable systems peaks result when a "worst case" test specimen is used. For

the Hall technique on biological specimens (7), a special specimen holder design may be necessary which creates a system peak which is used to characterize the specimen holder contribution to background counts (8). Low Z specimen grids and support washers are necessary, however Be grids often yield Fe peaks, nylon grids can yield Ti peaks, etc.

C. Limitations to Qualitative Analysis due to Sample Self-Fluorescence Effects

When thin samples are studied that have some remaining bulk material remote from the thin edge (ion thinned foils, electropolished foils, etc.) x-rays generated by BSEs, characteristic or continuum radiation in the bulk areas of the sample may be detected (2,3,4). This effect may be particularly insidious in systems that have elements in the analyzed volume with characteristic x-ray lines just above the critical excitation energy of elements in the bulk. Although the fluorescence effects may be small, the stray radiations striking the bulk areas may complicate analysis for small amounts of element B in an analyzed volume A contained within a matrix high in element B. Sample self-fluorescence effects are minimal in specimens such as small particles distributed on a carbon support film, or thin films with no bulk areas.

D. Limitations to Qualitative Analysis due to Sample/Detector Geometry

The EDS spectrum can be seriously affected by line-of-sight problems, where some portion of the sample or specimen holder subtends the x-ray beam from the analysis point, generally causing low energy x-rays to be preferentially absorbed over high energy x-rays. This problem is particularly probable in instruments with horizontally-mounted detectors where the detector axis intersects the point of analysis at right angles to the beam (4). It is necessary to assure that the specimen is properly tilted with respect to the detector (particularly if double-tilt holders are used), to optimize peak-to-background counts (2) and to give a free line-of-sight to the detector. Also, the specimen region near the analysis area should be inspected (perhaps using a secondary electron image) to assure that there are no large particles, bent film edges, or grid bars nearby which might cause absorption problems.

QUANTITATIVE ANALYSIS

A. General Comments

Quantitative EDS microanalysis suffers from the same limitations as qualitative analysis. However, given that sample self-fluorescence effects are vanishingly small (with proper choice of specimen), and system peaks are minimized, the analyst has to be concerned primarily about applying an appropriate method of quantification sufficient to produce relevant information about the sample. For absolute quantification, the Cliff-Lorimer ratio method (9) is most popular, but comparision of unknown spectra to thin film standards is also possible (10,11), and development of suitable working curves from analysis of standard compounds can yield accurate determinations of relative element ratio changes (12). Counting statistics dominate the accuracy of quantification. Spectra are obtained with no peak overlaps, accuracies to a few percent of the amount present can be obtained, provided enough counts are acquired in a spectrum, or enough spectra are analyzed. When there are severe peak overlap problems, the accuracy of quantification may be limited primarily by the nature of available deconvolution programs and how they are applied to unknown spectra (3). Simple Gaussian peak-fitting routines may not be sufficient, particularly if spectra have peaks whose shapes are non-Gaussian (due to effects such as incomplete charge collection which leads to tailing on the low energy side of the peak).

B. Additional Problems

EDS quantification of minor elements can be seriously affected by background problems. The bremsstrahlung contribution to an EDS spectrum arises not only from the analysis point, but also from the bulk regions surrounding the specimen, genererated by BSEs. The background may be relatively large when the specimen holder contains large bulk of low atomic number material. The background may also contain a contribution from high-energy BSEs which penetrate the detector window, dependent upon the detector geometry and AEM operating mode (13). The background affects quantification by decreasing P/B ratios (and thus counting statistics), and may cause problems with background stripping routines. It can seriously affect the accuracy of quantification when the Hall technique is used to determine compositions of biological tissues (8). The use of low-mass specimen holders which contain elements that

contribute a measurable characteristic peak for spectrum-scaling and subtraction purposes may improve analyses using the Hall method. It is also important to be aware of detector artefacts such as peak tailing, pulse pile-up effects, escape peaks, etc., all of which may influence the spectral intensities needed for quantitative analysis.

Absorption and direct fluorescence effects can become more serious as the sample thickness increases. The ratio technique (which requires a thin-film criterion to be met) must be modified to correct for these effects when necessary (2,3). The thin-film criterion for a particular system may be calculated and related to thickness. Direct thickness measurements may be necessary; alternatively, a plot of the ratio of intensities of low energy to high energy x-ray lines for a particular element relative to a measured Hall background region can often indicate when the thin-film criterion breaks down for a given measurement.

Crystal orientation effects can cause enhanced emission of particular x-rays (14). It is generally important to avoid highly diffracting specimen regions for this reason. When EDS analyses are conducted in STEM mode and highly convergent incident beam angles are used, the effect is minimized (14).

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