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MICROANALYSIS OF LIGHT ELEMENTS WITH AN
ULTRATHIN WINDOW X-RAY SPECTROMETER

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L. E. Thomas

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MICROANALYSIS OF LIGHT ELEMENTS WITH AN ULTRATHIN WINDOW X-RAY SPECTROMETER

L. E. Thomas

Hanford Engineering Development Laboratory, Richland, Washington 99352

Compared to electron energy loss spectrometry (ELS), energy-dispersive X-ray (EDX) spectrometry at first appears inefficient for microanalysis of light elements. K-shell ionization cross sections increase rapidly at low atomic numbers, as shown in Figure 1, while the corresponding X-ray yields remain about constant. Also, the efficiency of the EDX detector decreases at low X-ray energies (Figure 2) due to X-ray absorption in its inactive outer layers and protective window. Even if the window is eliminated, these considerations clearly favor ELS for detection of small, light element masses.

On the other hand, the advantages of EDX microanalysis over ELS for situations where ample X-ray quanta are produced make it desirable to extend this method at least to carbon. These advantages include high signal to background ratios, which means high sensitivity, and the ability to analyze specimens with thicknesses in the range (30 nm and up) normally encountered in materials applications. This paper describes an ultrathin window (UTW) X-ray detector designed to operate on a 100 kV analytical TEM/STEM (JEOL Model 100CX) and compares its performance with that of a magnetic sector electron spectrometer (JEOL EA-2) on the same microscope.

The UTW detector shown in Figure 3 was designed by R. G. Musket of Kevex Corporation to operate with a vacuum and light tight window, consisting of 0.1 μm thick Parylene-N⁽⁴⁾ and 0.1 μm thick vapor-deposited aluminum, in place of the conventional 7 μm beryllium window. To protect the window during specimen insertion, the detector assembly retracts through an O-ring sliding seal and is isolated behind a gate valve where its vacuum is maintained by ion pumps. The detector itself is a 10 mm² x 2 mm thick Si(Li) crystal which was selected for optimum energy resolution and X-ray efficiency (Figure 2 shows the calculated efficiency for the detector/window combination), and matched to the preamplifier and amplifier for low noise. Although the window can easily be changed, this has not been necessary in seven months of operation.

Figure 4 illustrates the detection of light elements carbon through silicon (neon excepted) and the resolution of adjacent K X-ray peaks with the UTW detector. The spectra were obtained from 50 to 100 nm thick "dust" particles of BN, MgF₂, NaF, Al₂O₃ and SiO₂ on carbon films in 100 second counting times with a 10 nm diameter electron beam. Energy resolution of the UTW detector, measured as the full width at half the peak maximum from non-overlapped peaks varied from 98 eV for carbon to 110 eV for aluminum. Boron was not detected; the peak extending from zero energy is produced by electronic noise. Also, the small Cu-L peak at 928 eV is due to continuum fluorescence of the copper support grids. The spectrum from a 50 nm thick MgO cube shown in Figure 5 illustrates the very low continuum background below 1 keV for the UTW detector with 90° X-ray takeoff. The X-ray peak to background (P/B) ratios for O-K and Mg-K in this case were 20 and 35, respectively. ELS microanalysis of the same MgO crystal gave oxygen and magnesium P/B ratios of only 0.3 and 0.05; in fact, the Mg-K edge was barely detectable. Although the spectrum in Figure 5 also shows very low carbon contamination, contamination from specimen sources was difficult to avoid during microbeam analyses and affected ELS and EDX analyses equally.

Comparison of ELS and EDX spectra from boron nitride (in Figure 6) shows the advantages of ELS in energy resolution and detection of very light elements. High resolution could be important in separating overlapped K-peaks from light

L. E. Thomas

elements and L-peaks from transition metals. On the other hand, the EDX method also allows analysis of the well-separated K-peaks from these metals. Note that the spectra in Figure 6 were taken from particles of different thickness to emphasize the best features of each method.

For microanalysis of specimens sufficiently thin that X-ray absorption and fluorescence in the specimen are negligible, ratios of integrated intensities for pairs of elements (1 and 2) are commonly related to mass concentration ratios by an equation such as⁽⁵⁾

$$\frac{C_1}{C_2} = k_{12} \frac{I_1}{I_2}$$

The k-factors may be obtained from EDX intensities measured from the samples with known concentration ratios, or calculated from the ionization cross sections (σ), fluorescent yields (ω), atomic weights (A) and detector efficiencies (η) as

$$k_{12} = \left(\frac{\sigma\omega\eta}{A} \right)_2 / \left(\frac{\sigma\omega\eta}{A} \right)_1 ,$$

(assuming unresolved K X-ray peaks for light elements). Figure 7 shows experimentally determined and calculated k-factors relative to Si-K for the UTW detector. The experimental k-factors for O, F, Na, Mg, Al and Si were obtained crudely from EDX intensity measurements of 50-100 nm thick MgO, Al₂O₃, SiO₂, MgF₂ and NaF particles (which probably did not meet the thin specimen criterion). Comparison of the calculated and experimental k-factors indicates that the UTW detector should have better sensitivity for light elements than is observed. A likely explanation for the difference is that a carbon layer 1 to 2 μ m in thickness has formed on the Parylene/Al window. K-factors were also measured carefully for Al, Si, Ti, Cr, Fe and Ni with the UTW detector, using alloy standard specimens. Except for the lighter elements, these results, also shown in Figure 7, agree with published k-factors⁽⁶⁾ for a standard (beryllium window) detector.

The UTW X-ray detector in analytical electron microscopy provides a needed capability for analyzing all elements down to carbon in specimens 30 nm and up in thickness. This detector provides adequate energy resolution to resolve adjacent K X-ray peaks from light elements and, with care, can be operated for long periods without changing windows. Energy loss spectroscopy can detect elements at least down to lithium, measure smaller masses of light elements than EDXS, and may provide chemical bonding information, but it is limited to very thin specimens.

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Fig. 1.
K-shell ionization cross sections, (1) fluorescent yields (2) and calculated K X-ray yields for light elements.

Fig. 2.
EDX detector efficiencies calculated for X-ray absorption (3) in inactive detector and window (4) layers.

Fig. 3.
Ultrathin window EDX detector assembly on 100 kV TEM/STEM. Detector retracts behind gate valve for complete vacuum isolation.

Fig. 4.
Superposition of light element spectra obtained with UTW detector from 50 to 100 nm thick BN, MgF_2 , NaF, Al_2O_3 and SiO_2 particles on carbon film (Cu support grid).

Fig. 5.
EDX spectrum from 50 nm thick
MgO crystal (MgO smoke on
copper grid). The peak to
background ratio is 20 for
O-K X-rays and 35 for Mg-K
X-rays.

Fig. 6.
ELS and EDX spectra from
boron nitride. The spec-
tra were obtained from
different particles.

Fig. 7.
Cliff-Lorimer k-factors cal-
culated and measured for
light elements with the UTW
detector. K-factors mea-
sured with a standard (Be
window) detector(6) are
shown for comparison.