Combined Electron Excitation and X-Ray Excitation for Spectrometry in the SEM

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Introduction

Energy-dispersive X-ray spectrometry (EDS) is an analytical technique used to determine elemental composition. It is a powerful, easy-to-use, non-destructive technique that can be employed for a wide variety of materials. In this technique the electron beam of the scanning electron microscope (SEM) impinges on the sample and excites atomic electrons causing the production of characteristic X rays. These characteristic X rays have energies specific to elements in the sample. The EDS detector collects these X rays as a signal and produces a spectrum. Samples also can be excited by X rays. Collimated and focused X rays from an X-ray source produce characteristic X rays that can be detected by the same EDS detector. When X rays are used as the source of excitation, the method is then called X-ray fluorescence (XRF) or micro-XRF.

Generally, SEM/EDS analysis takes place at an excitation energy of 20 keV. This method can detect most elements that are present in amounts above 0.1 wt% (1000 ppm). However, in terms of detectability, electron excitation is best suited for light elements with X-ray energies below 2 keV. X-ray excitation allows detection of the heavier elements at concentrations lower than can be seen with SEM/EDS. In fact, for X rays above 2 keV, XRF can detect elements down to levels under 100 ppm.

The complementary advantages of these techniques have been reviewed several times [1, 2]. Electron beam excitation is better suited to imaging and microbeam quantitative compositional analysis and maps. XRF is better suited to quantitative analysis of trace elements but over a much larger area. Unlike the electron-beam excitation of the SEM, X-ray excitation produces spectra with little or no background. The lack of bremsstrahlung background increases the detectability of peaks from elements at low concentrations that otherwise might be lost in the background. Also, with an X-ray source, there is no need to coat the sample because charging is virtually non-existent when using X-ray photon excitation. This article describes how these two techniques can be used together for combined analysis in the same SEM.

Methods and Materials

An analyst can take advantage of the fact that most SEM/EDS microanalysis systems already have a high-quality EDS detector, with an ultra-thin window that allows the analysis of light elements. Thus, to enable good-quality XRF within an SEM, one only needs a suitable X-ray source. The combined system provides both XRF and electron-beam X-ray spectrometry within the same chamber, *in vacuo* or in air, as appropriate for the sample.

Early work. Previous attempts have been made to add XRF to an SEM using standard EDS detectors already in place [3]. Most of these methods used the electron beam to create the fluorescing X rays with a thin transmission-target foil placed between the beam and the sample. The main problem with this approach was the low incident X-ray flux onto the sample, especially if the analysis area was restricted. The advantages of XRF—improved sensitivities and higher peak-to-background ratios—were difficult to achieve because of the low count rates.

This problem has been solved by attaching a separate X-ray source to the SEM, which can produce X-ray fluxes orders of magnitude higher than those achieved with low-current SEM beams and transmission foils. By restricting the sample analysis area with apertures or active focusing optics, one can achieve count rates from relatively small beam spots that are typical of standalone micro-XRF spectrometers (for example, on a stainless steel specimen a 10 µm X-ray spot can yield > 2,000 counts per second, whereas a 40 µm spot can yield > 20,000 cps) with all the advantages of the XRF technique [4].

X-ray tubes added to the SEM. Figure 1 shows the first XRF implementation: a re-entrant close-coupled low-power (3–4 W) transmission-target tube (*f*X™) with an integrated aperture assembly that collimates the X-ray beam to about 0.5 to 5 mm, depending on the aperture. Generally a silver target is used, however this can be changed to best suit the needs of sample analysis. This tube can operate up to 35 kV and does not require any active cooling. An internal cross-sectional drawing for mounting of the small spot *f*X™ X-ray tube is shown in Figure 2.

Figure 3 shows a second implementation: an X-Beam™ assembly, which is a combination of a medium-power X-ray tube (up to 50 W) with an integral polycapillary optic that

Figure 1: Small-spot *f*X™ X-ray tube, producing a spot size of 0.5–5 mm on the sample, attached to an SEM.

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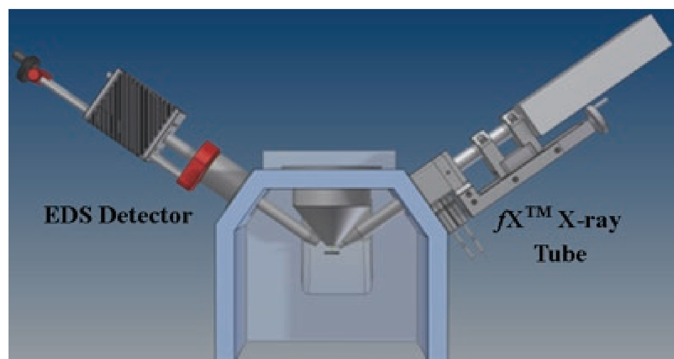

Figure 2: Diagram of small-spot *f*X™ X-ray tube attached to an SEM, also showing EDS detector.

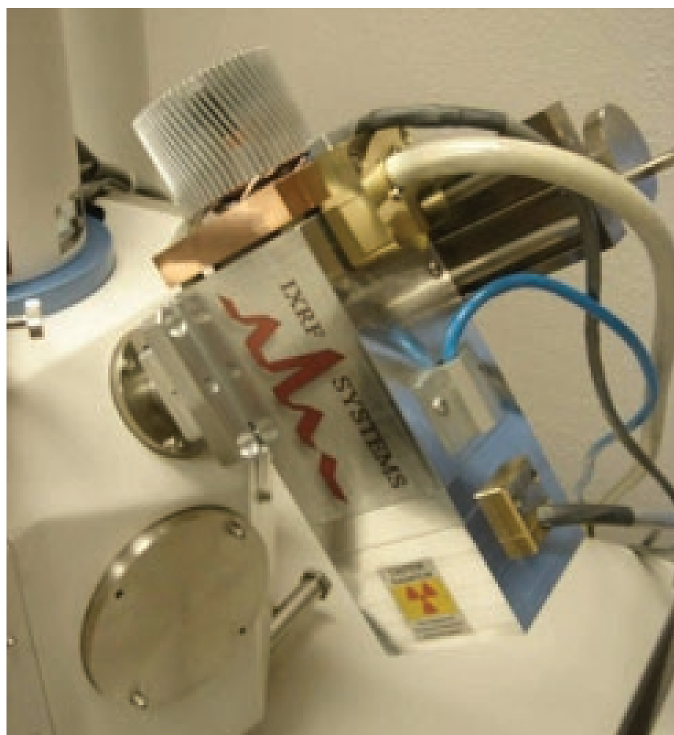

Figure 3: X-Beam™ X-ray source with a polycapillary focusing optic shown attached to an SEM.

focuses the X-ray beam down to about 10–40 μm at the sample. Generally a rhodium target is used, however this can be changed to best suit the needs of sample analysis. In addition, this source has an integral shutter so the beam can be on continuously, even if the SEM chamber is opened. An integral air-cooling system is available for operation at the highest power (50 keV, 1 mA).

Modes of operation. Typical SEM techniques can be readily adapted for use with an X-ray tube source, including spot mode, line scan, and stage scanning to acquire elemental maps from either beam source. Software already exists for SEM automation and EDS analysis, and now the quantitative XRF algorithms have been integrated. The result is a compact dual-purpose instrument for imaging and quantitative analysis of a variety of sample types. Both X-ray source configurations discussed above have been implemented without any interference with the normal SEM operation.

Results

Micro-XRF in the SEM is able to identify and quantify the heavier elements (atomic numbers Z > 11) at very low levels of concentration. Figure 4 shows an XRF spectrum of a NIST 612 glass containing a variety of elements across the periodic table at concentrations between 16–78 ppm. The low concentrations shown of the trace elements revealed in Figure 4 could never be detected with electron excitation alone. However, electron excitation is better than X-ray excitation for detecting the light elements. These two techniques can be combined to fully analyze a sample that contains both light and heavy elements.

Figure 5 shows both electron- and X-ray-excited spectra for a NIST 610 glass standard. The glass standard includes many heavier elements at low concentrations. The two spectra were collected from the same area of the specimen. The top spectrum is the electron-excited spectrum, and the bottom spectrum is the XRF spectrum. As these spectra show, electron-excited analysis identifies the lighter elements of oxygen, sodium, and silicon; but above 2 keV the only element detected is calcium at 12 wt%. However, the XRF spectrum shows many elements that were not detected with electron excitation. The heavier

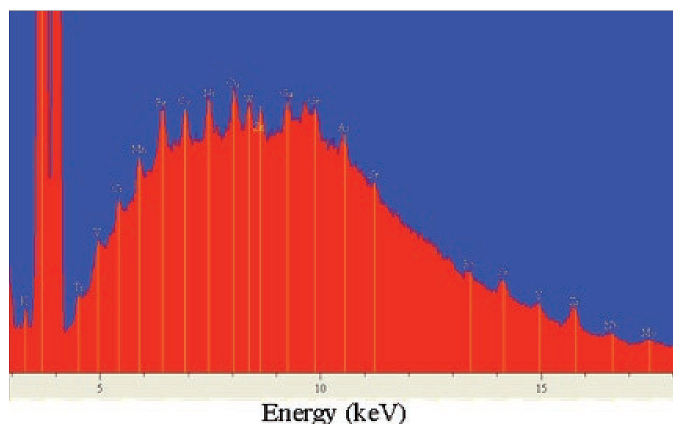

Figure 4: Spectrum from X-Beam™ analysis of NIST 612 Glass Standard operated at 50 keV and 1 ma. The acquisition time was 120 minutes.

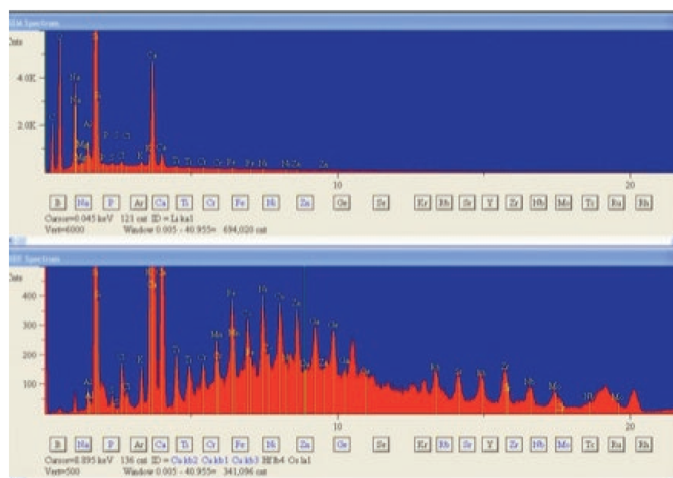

Figure 5: A dual-analysis spectrum collection from a NIST 610 glass standard. (top) Electron excitation, (bottom) XRF spectrum excited by an X-ray tube. The horizontal axes of the spectra energy (keV). These spectra were collected with rhodium target X-Beam™ at 50 keV and 1 mA.

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elements Zn through Bi detected by XRF were present in concentrations ranging from 300 ppm to 900 ppm. Conversely, the XRF spectrum does not detect the lighter elements of oxygen and sodium. By combining the two excitation methods, a complete analysis can be accomplished.

To fully understand the advantages of this method, minimum detection limits (MDLs) may be calculated using the following equation [5]:

$$MDL = \frac{3.29\sqrt{B}}{S \cdot t}$$

In above equation S is the signal strength (counts/s), t is the acquisition time (s), and B is the number of background counts. Table 1 shows the results of such calculations for trace elements in an aluminium alloy where the MDLs for most of the trace elements are below 100 ppm.

The combined analysis can be taken one step further to combined quantification. Traditionally, electron-excited EDS X-ray analysis is quantified using the ZAF quantification method [5]. XRF analysis is quantified using fundamental parameters (FPs) for analysis [5]. The relationship between these two quantitation methods (ZAF and FP) is not known. Thus, to achieve combined quantification, the two methods cannot be normalized by intensities alone. They must be normalized by k-ratio, which is the ratio of element intensity in the specimen to that from the pure element. Normalizing k-ratios was done iteratively at the same time as the normalization of concentrations. A partial sum was calculated for each method, and the sum of elements by these methods was set equal to one. These iterations allow for total quantitative analysis of light and heavy elements on one instrument. A dual quantitative analysis for 2014 aluminium is also shown in Table 1.

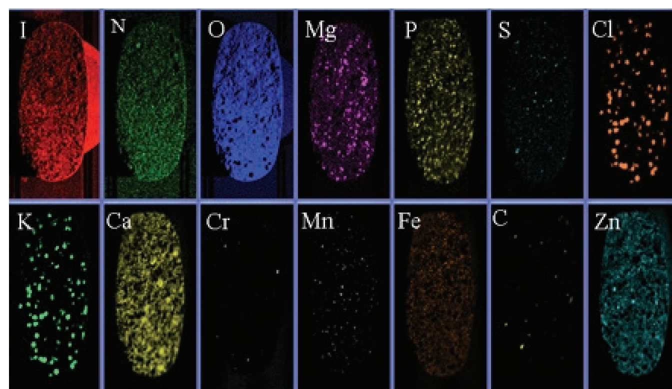

Figure 6: Elemental maps of a multi-vitamin, collected simultaneously with electron-beam excitation (top row: C, N, O, Mg, P, S, and Cl) and X-ray excitation (bottom row: K, Ca, Cr, Mn, Fe, Cu, and Zn).

Mapping is yet another tool that is enhanced by the addition of micro-XRF to the SEM. Both electron and X-ray excitation can be used for elemental mapping. When mapping with the electron beam of the SEM, usually the beam is rastered over the sample to collect the map. Conversely, the X-ray beam is mounted in a stationary position on the SEM; so the sample must be moved under the X-ray beam using the specimen stage. The following figures show some examples of X-ray mapping, using the SEM x-y stage to move the sample under both the X-ray source and the stationary electron beam. Figure 6 shows multiple elemental analysis maps of a multi-vitamin. The electron beam and the X-ray source were used to collect elemental maps for both light and heavy elements simultaneously.

Figure 6 shows that the maps not only indicate the elements present but also their distribution and relative intensities. Electron-beam excitation mapped the lighter elements of oxygen, nitrogen, carbon, magnesium, phosphorus, sulphur, and chlorine. X-ray excitation produced maps of potassium, calcium, chromium, manganese, iron, copper, and zinc. Relative locations of elements also can be displayed in elemental overlays (Figures 7 and 8).

Table 1: Quantitative data for dual analysis of 2014 aluminum alloy. Electron beam excitation (20 keV, 62 µA) for elements up to Si and X-ray excitation (50 kV, 1 mA) for elements above Si.

Element	Line	Intensity (c/s)	Quant	Conc (wt%)	MDL (wt%)	MDL (ppm)
Mg	Kα	41.36	ZAF	0.479	0.039	390
Al	Kα	7079.86	ZAF	91.694	0.043	430
Si	Kα	8.19	ZAF	0.848	0.045	450
Ti	Kα	4.47	FP	0.085	0.007	70
Cr	Kα	7.00	FP	0.076	0.006	60
Mn	Kα	17.40	FP	0.631	0.060	600
Fe	Kα	8.49	FP	0.345	0.065	650
Ni	Kα	19.86	FP	0.100	0.005	50
Cu	Kα	1234.69	FP	5.346	0.004	40
Zn	Kα	18.94	FP	0.071	0.004	40
Ga	Kα	17.33	FP	0.076	0.004	40
Zr	Kα	9.79	FP	0.034	0.004	40
Sn	Kα	4.67	FP	0.089	0.024	240
Pb	Lα	9.46	FP	0.060	0.006	60
Bi	Lα	5.61	FP	0.033	0.006	60

Conclusion

EDS using electron excitation in the SEM is a powerful analytical technique; however, this technique can be complemented, and hence improved, with the addition of micro-X-ray fluorescence. Electron excitation is best suited for analyzing the lighter elements below sodium on the periodic table, whereas X-ray excitation is best suited for elements heavier than sodium. X-ray fluorescence produces spectra with little or no background and also allows for parts-per-million

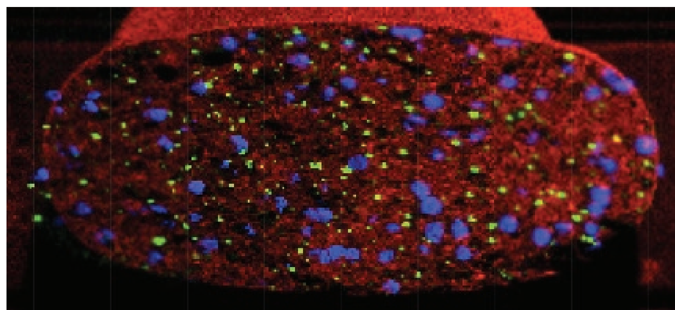

Figure 7: Elemental map overlay of multi-vitamin: carbon (e-beam)—red, manganese (XRF)—green, and potassium (XRF)—blue.

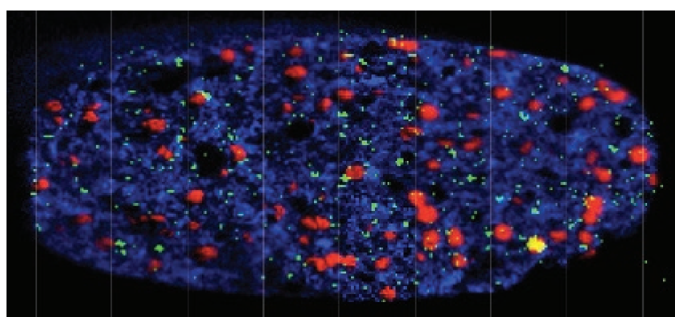

Figure 8: Elemental map overlay of multi-vitamin: chlorine (e-beam)—red, sulfur (e-beam)—green, and zinc (XRF)—blue.

elemental detection above sodium. The addition of an X-ray tube to the SEM/EDS system allows combined use of both techniques, on the same sample at the same time.

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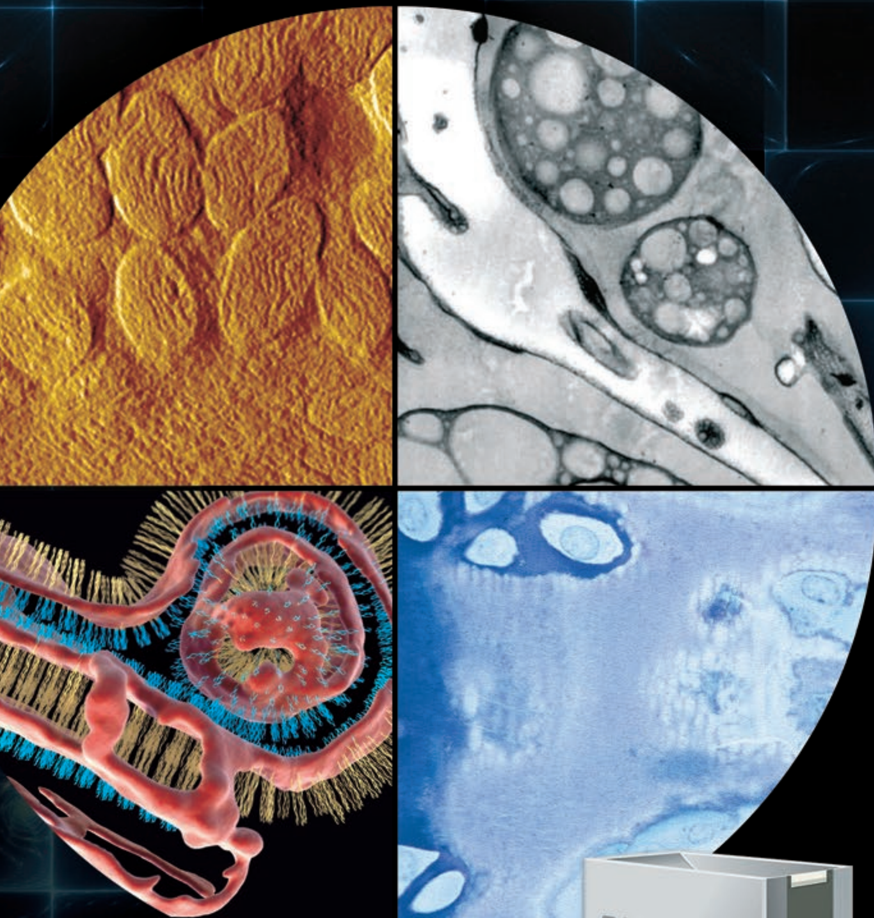

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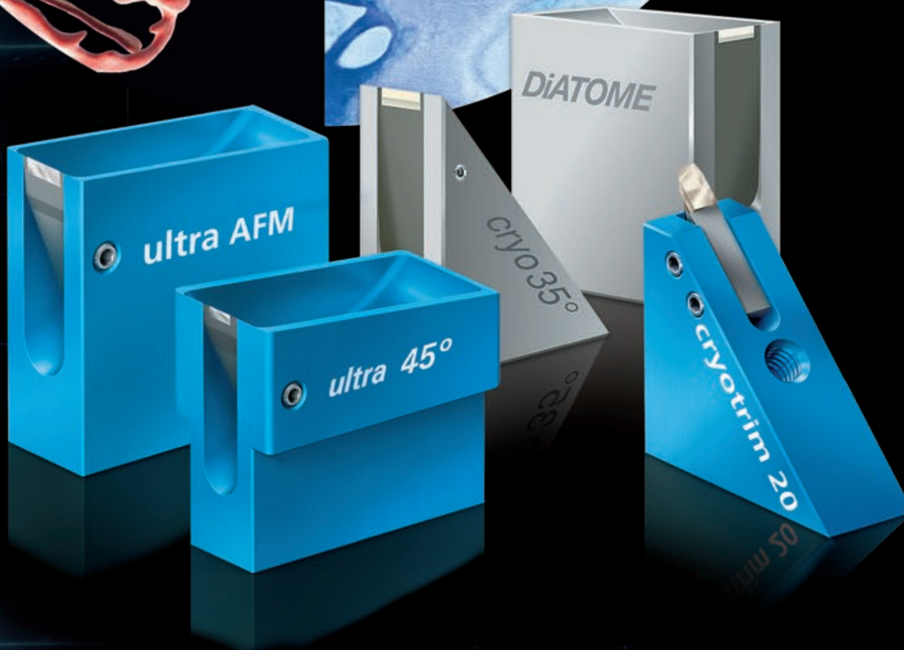

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