µ-XRF Analysis on ZEISS Scanning Electron Microscopes

Application Note

Introduction

A large number of ZEISS Scanning Electron microscopes (SEM) like the EVO®, SUPRA™ and ULTRA are currently used not only for excellent imaging but also as sophisticated analytical instruments. One of the most widespread analytical methods on the SEM is Energy Dispersive X-ray spectroscopy (EDS). However, with a detection limit of around 0,1% for most elements its sensitivity is often not sufficient for detection of trace elements. The reason for the limited trace sensitivity in bulk materials is the high Bremsstrahlung background, typical for electron excitation. A method to improve EDS performance on the SEM is to use X-rays for excitation. X-ray excitation considerably reduces the background, although with reduced lateral resolution.

Fig: 1: iMOXS µ-XRF mounted on an EVO® 40 chamber EDS port.

Polycapillary X-ray optics open up new possibilities to focus X-ray radiation of an X-ray tube onto small spots with a diameter of several tens of microns. Use of tapered monocapillaries reduces the spot size even further down to 10 µm, however at the cost of excitation intensity. The reduced intensity can be partially compensated by larger measurement times. This enables material analysis of microvolumes with much higher sensitivity for trace elements. The technique has already been successfully introduced as Micro-Beam X-ray fluorescence. By introducing µ-XRF with an X-ray excitation source including capillary optics in a ZEISS SEM, the generated characteristic fluorescence radiation can be analysed by the typically available EDS system on a SEM (Fig. 1). Compared to electrons, X-rays are not sensitive to low vacuum. Therefore accurate µ-XRF analysis measurments can be performed within Variable Pressure (VP), eXtended Variable Pressure (XVP®) and Extended Pressure (EP) in the specimen chamber and also without coating for non-conductive specimen.

Instrumentation

The iMOXS system developed at the IfG - Institute for Scientific Instruments GmbH consists of:

- a low-power microfocus X-ray tube with attached X-ray optics
- up to 4 optional primary filters for optimising the excitation spectrum
- support for adaptation of the X-ray source to the SEM
- a control and high voltage supply unit (CSU) manually or PC operated
- Windows® programs for operating the CSU and for quantitative analysis of bulk and film samples

The maximum high voltage is 50 kV which leads to a maximum power of 30 W. Different anode materials like Cr, Cu, Mo, Rh, Pd, W are available depending on customer needs. The spot size with capillary optics is in the range ~50 µm to 300 µm. The system in combination with the ZEISS SEMs meets all the demands of X-ray safety regulations.

Analytical properties

The X-ray excitation option significantly reduces the con-tinuous (Bremsstrahlung) background and improves sensi-tivity by a factor of 20-50 due to the better peak-to-background ratio. The penetration depth for X-rays in a specimen is larger than for accelerated electrons. As a result, in the case of homogeneous bulk specimens, larger volumes are excited, which leads to a more representative analysis. In the case of thin film samples, thick layers and multilayer structures can also be analysed.
A great advantage is the ability to analyse non-conductive specimen without a conductive coating. This reduces specimen preparation time considerably and removes any artefacts in the spectrum caused by coating. In addition, porous specimen can be analysed without any charging problems. Simultaneous availability of electron and X-ray excited spectra gives the possibility of evaluating and combining information from both methods, i.e. excitation of light elements together with high sensitivity for trace elements.

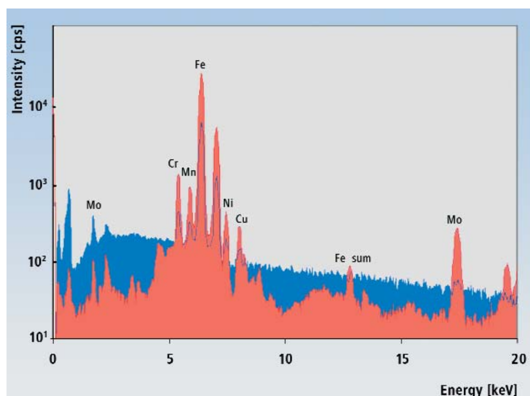

Fig. 2: Spectrum of a steel sample excited with an X-ray (red) and electron (blue) beam.
Courtey of Institute for Scientific Instruments GmbH, Berlin.

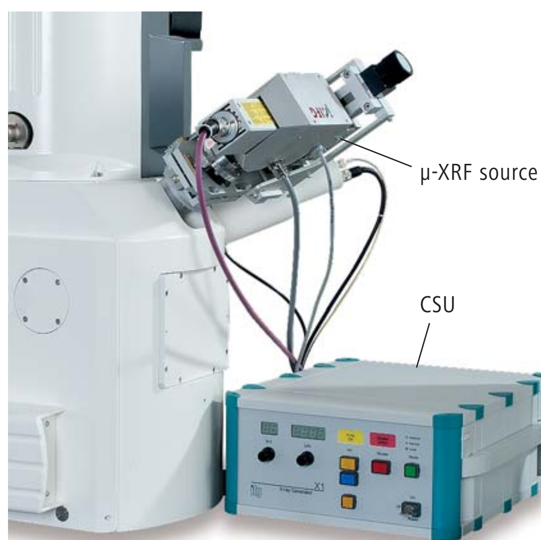

Fig. 3: iMOXS µ-XRF source with Control and high voltage Supply Unit (CSU).

When the radiation of an X-ray tube is used for excitation, the Bremsstrahlung radiation is absent and the peak-to-background ratio is considerably improved. The primary X-ray beam however, can be scattered in a specimen and generate a continuous background. This scattering depends on the measurement geometry as well as on the specimen itself. The lighter the specimen material is, the stronger the scattering is. The higher peak-to-background ratio leads to significantly improved minimum detection limits.

Application examples

1. Analysis of a stainless steel alloy

Fig. 2 presents two spectra measured with a stainless steel specimen under similar excitation conditions (excitation energy, impulse rate). The electron excited spectrum (blue) clearly reveals the higher background in comparison to the X-ray excited spectrum (red). As a result, elements with low concentrations are difficult to identify with electron excitation. By comparison, X-ray excitation of heavy elements is more effective, so that their fluorescence intensities are noticeably higher.

2. Analysis of an aluminium alloy

The spectra presented in Fig. 4 were measured with an Al-alloy specimen. Although the light matrix causes

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We make it visible.

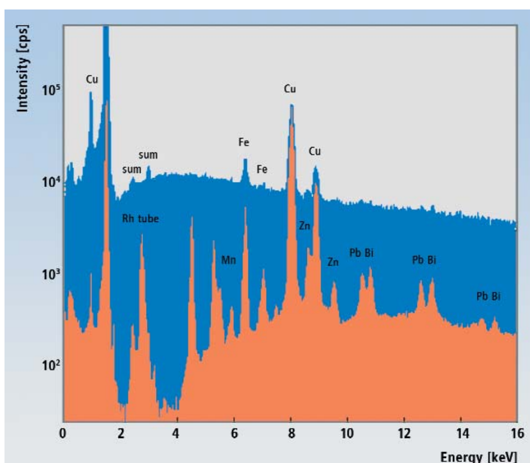

Fig. 4: Spectra of an Al specimen excited with an X-ray (red) and electron (blue) beams both excited with 30kV.
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relatively strong scattering of the primary X-ray radiation, the difference in backgrounds of both spectra is clearly visible. The X-ray excited spectra show a considerably larger variety of characteristic lines, which can be assigned to the elements with low concentration. In the case of the electron excitation these lines are also excited, but overlap partially with the high spectral background. This leads to better minimum detection limits for the X-ray excitation. A brief summary of the minimum detection limits for some elements in Fe and Cu alloys is presented in Table 1. The excitation voltages during these measurements were both 30kV for the electron beam excitation and the X-ray excitation with an X-ray tube.

Element	X-ray	Electron
Ti	100	1000
Cr	80	800
Mn	50	800
Fe	40	800
Ni	30	900
Cu	20	1000
Mo	200	2000
Sn	300	4000
Pb	200	5000

Table 1: Minimum detection limits in µg/g for X-ray and electron excitation of steel and aluminnium alloys.

3. Analysis of glass

Scattering of the primary X-ray beam on glass is comparable with that in Al alloys. This was confirmed experimentally with the multi-element standard NIST 610. The glass in this standard contains a series of different elements with concentrations of approx. 500µg/g for each element. Both spectra in Fig. 5 reveal again a reduced background for the X-ray excitation (red spectrum) and consequently the possibility of identifying trace elements in the sample. Minimum detection limits, calculated on the basis of these measurements, are summarised in Table 2.

Element	LOD
Ti	50
V	40
Cr	30
Fe	25
Ni	25
Cu	25
Zn	20
Pb	30
Rb	15
Sr	15

Table. 2: Minimum detection limits in µg/g for trace elements in glass.

In addition, comparison of both spectra clearly shows that excitation with an X-ray beam is more effective for the high-energy fluorescence lines, i.e. heavy elements can be identified better. Besides, in the case of X-ray induced analysis of non-conductive samples, e.g. glass, sample preparation becomes easier, because preliminary conductive coating is not necessary and there are no added peaks the coating material.

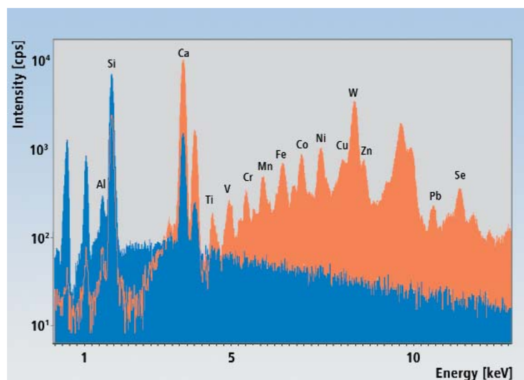

Fig. 5: Spectra of the glass standard NIST 610 excited with an X-ray (red) and electron (blue) beam.
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More Information on the iMOXS source:
www.ifg-adlershof.de

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