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Quantitative Trace Analysis with X-Ray Fluorescence in the Scanning Electron Microscope

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Abstract. The potential of a scanning electron microscope will be enhanced markedly by adapting the X-ray fluorescence for material analysis. The illuminating system "röntgenbox" enables the analyst to execute analyses in the concentration range from 100 percent down to the low ppm range without time consuming preparation steps. X-ray intensities of traces are measured for different anodes in the elemental range from $Z = 11$ to 90 (sodium to thorium).

Key words: röntgenbox, scanning electron microscope, trace analysis, X-ray fluorescence, X-ray intensity.

Electron Excitation and X-Ray Fluorescence

In the scanning electron microscope (SEM) the electron beam is usually directed straight onto the sample surface. At the point of impact not only electrons but also X-rays are emitted. The X-radiation enables the analyst to execute a non-destructive material analysis. Illuminating the sample with X-rays, X-radiation is generated too, but without the large amounts of continuous bremsstrahlung, caused by the decelerating electrons. X-ray fluorescence (XRF) with its low spectrum background permits, therefore, also trace analyses in the ppm-range, where the weak X-ray signals of smaller contents are clearly detectable because of the low intensity of continuous X-radiation. A comparison of both analysis methods in the SEM is listed in Table 1. According to Table 1, X-ray fluorescence enhances the potential of a SEM.

The measurements given in the following were executed with the illuminating system "röntgenbox" (Fig. 1). Instead of an earlier construction with massive anodes [1, 2], the new construction is equipped with a set of plug-in foil anodes, providing an optimum X-ray excitation in most cases [3—5].

Table 1. Comparison of electron excitation and XRF for the combination of a scanning electron microscope and an energy dispersive X-ray spectrometer

	Electron excitation	X-ray fluorescence
Local resolution	1 μm	100 μm
Information depth	1 μm	10–100 μm
Detection limit	300 μg/g	≤5 μg/g
Metallization of insulating samples required?	yes	no
Analyses of wool, glasses, powders?	no	yes
Measuring the thickness of surface coatings?	no	yes
Quantitative trace analysis?	no	yes

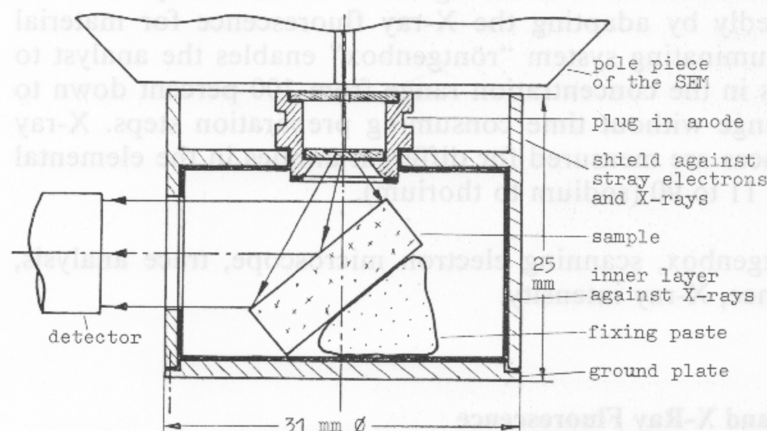

Fig. 1. The röntgenbox, cross section. The electron beam excites X-radiation in an anode, which illuminates the sample

The X-Ray Signal

In the widely used energy dispersive spectrometer (EDS) the X-ray signal is given as a number of counts in the channels of a multichannel analyzer. The net signal amounts to

$$N_{\text{net}} = N - N_B \quad (1)$$

with N_B as the number of counts in the spectrum background in the respective energy interval. Often the background as a function of energy is a straight line (Fig. 2), so N_B is simply given as

$$N_B = (N_{B1} + N_{B2})/2 \quad (2)$$

with N_{B1}, N_{B2} the background counts in equal energy intervals at both sides of the signal. With a curved background shape or signal overlap the net

signal results after subtraction of a reference spectrum, see Fig. 3. In a real analysis, the net signal is

$$N_{net} = S \cdot I \cdot t \cdot a \tag{3}$$

with S element intensity, I electron beam current on the anode, t analysis time, a sensitivity factor of the set up.

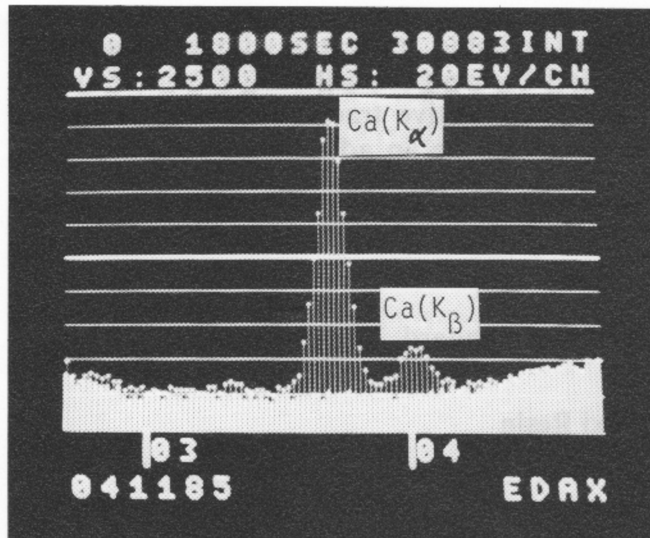

Fig. 2. X-ray spectrum of epoxi with 1000 ppm calcium. XRF with 5 μm thick molybdenum anode at 20 kV (shaded). White: Reference spectrum of pure epoxi

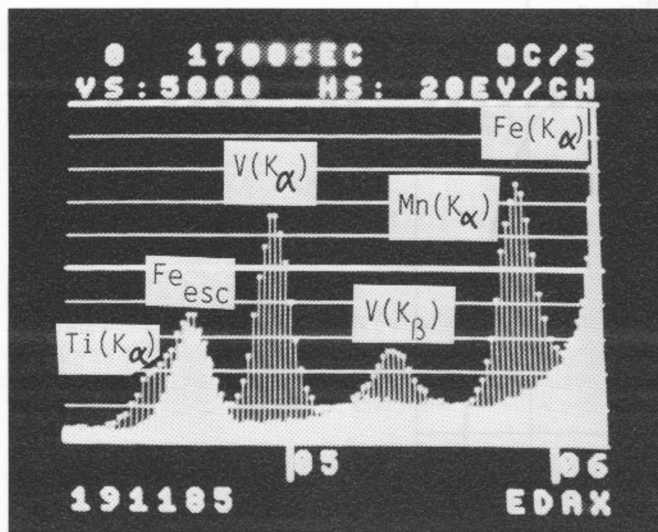

Fig. 3. Spectrum of iron with 2000 ppm titanium, 6200 ppm vanadium and 6800 ppm manganese. Note the escape peak near Ti(K_α), caused by fluorescence of the silicon material of the EDS detector by the intensive iron line Fe(K_α)

Trace Analysis

In common XRF material analysis the different material contents influence each other mutually by absorption and fluorescence. In trace analysis with concentrations in the range up to 0.1%, the radiation of the main material is nearly independent from the traces. Here the X-ray intensity of traces is directly proportional to their concentration,

$$S' = c \cdot S \tag{4}$$

with S' measured signal intensity, c concentration of the trace, S element intensity.

Therefore the measurement of suitable standards with certified trace concentrations provides the required element intensities $S(Z)$ with Z atomic number. With these intensities a quantitative trace analysis of unknown samples is executed easily. Often it will be an advantage to calculate the minimum detectable concentration c_{mdl} according to [6],

$$c_{\text{mdl}} = \frac{3\sqrt{N_B}}{N_{\text{net}}}\, c_0; \tag{5}$$

c_0 trace concentration in the certified standard.

Trace Element Intensities in Epoxi Resin

The element intensities $S(Z)$ and the corresponding c_{mdl}-values were measured with certified standards of glass, aluminum and iron. Further, a complete set of trace elements in epoxi resin was prepared and tested. Here

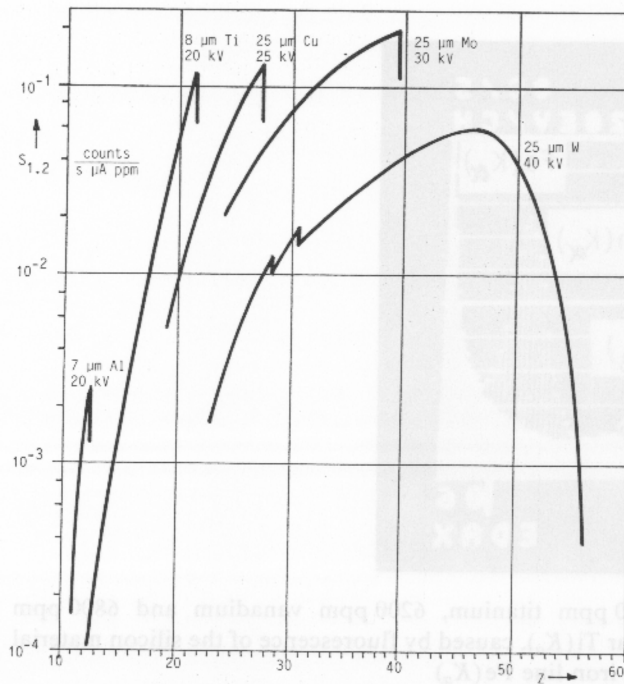

Fig. 4. Signal intensities for traces in epoxi. The element intensities for *K*-lines are given for different anodes, spreading the element range from sodium to barium

the trace elements were added as powdered chemical compounds, mostly oxides, to the viscous epoxi resin (UHU plus®). After curing, the epoxi surface was scraped to avoid X-ray absorption in the blank surface layer. The advantage of epoxi resin as main material is its only weak X-ray absorption with no X-ray lines in the range above 1 keV. So X-ray intensities are influenced by the main material to a limited extent only. Figs. 4 to 7 show the results. The element intensities for the *K*-lines from $Z = 11$ to 56 (sodium to barium) spread over $S = 10^{-4}$ to 10^{-1} counts/(s · μA · μg/g), well suited to detect also low concentrations. The index 1.2 at $S_{1.2}$ here only indicates the element dependent optimum energy range to acquire the signal by the EDS (= 1.2 × full signal width at half maximum). The *L*-line intensities reach only up to 10^{-2} counts/(s · μA · μg/g), so it is more favorable in most

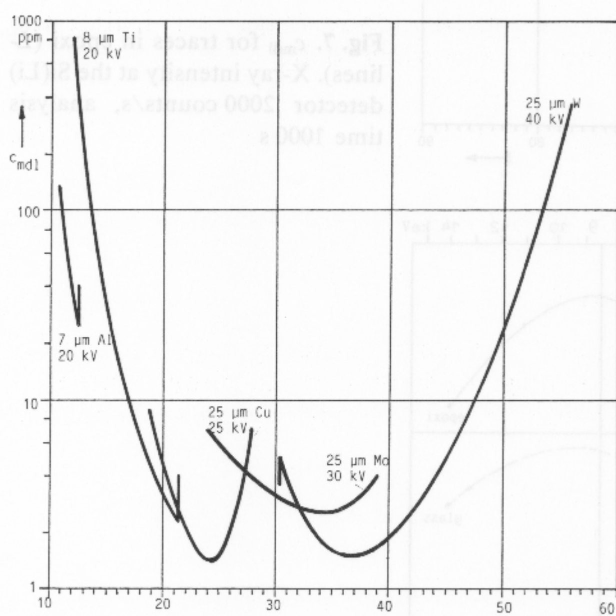

Fig. 5. Minimum detectable concentrations for traces in epoxi resin. X-ray intensity at the Si(Li) detector 2000 counts/s, analysis time 1000 s

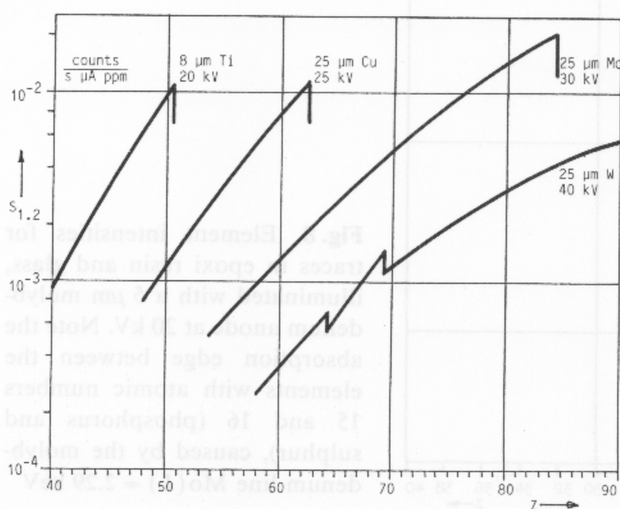

Fig. 6. Signal intensities (*L*-lines) for traces in epoxi resin. The element range is covered from zirconium to uranium

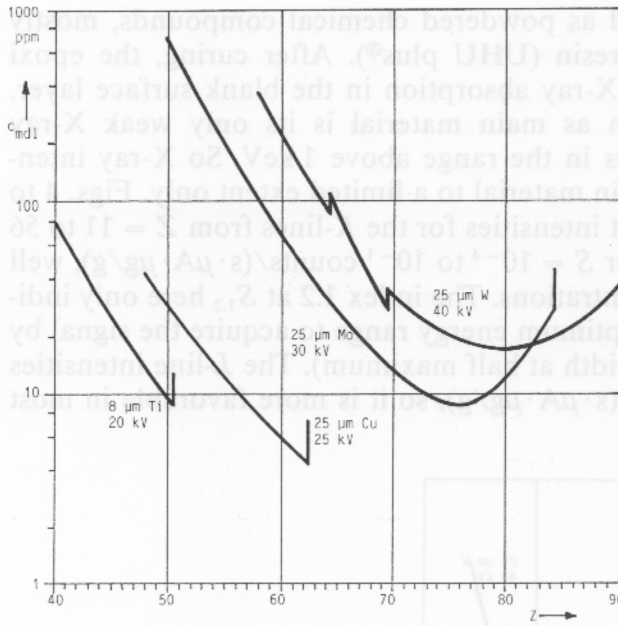

Fig. 7. c_{mdl} for traces in epoxi (*L*-lines). X-ray intensity at the Si(Li) detector 2000 counts/s, analysis time 1000 s

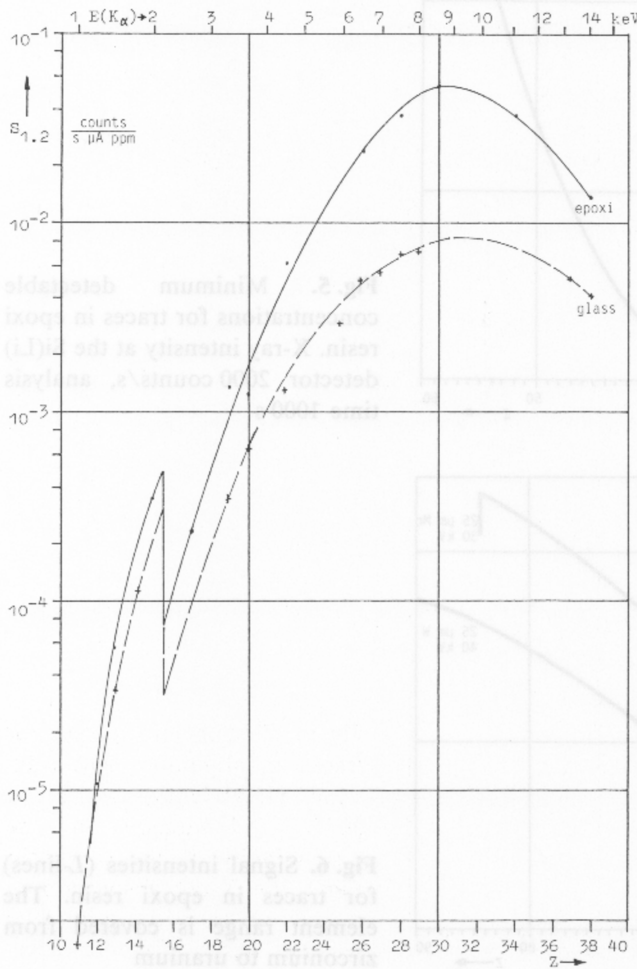

Fig. 8. Element intensities for traces in epoxi resin and glass, illuminated with a 5 μm molybdenum anode at 20 kV. Note the absorption edge between the elements with atomic numbers 15 and 16 (phosphorus and sulphur), caused by the molybdenum line $\mathrm{Mo}(L) = 2.29$ keV

cases to take the *K*-lines if possible. The c_{mdl} in Fig. 5 is in the range 100 to 1 μg/g for *K*-lines respectively 100 to 10 μg/g for *L*-lines in Fig. 7.

To transfer the $S(Z)$-curves to another set up of XRF in the SEM, several pure element sheets were measured with the conditions given in Table 2.

Table 2. Signal intensities for 15 × 15 mm² metal sheets to transfer the trace element intensities to an XRF set-up with other geometry and detector sensitivity

Anode	Voltage/kV	Metal sheet	Line	$S'_{1.2}$ in counts/s · μA
8 μm titanium	20	Silicon	K_α	540
25 μm copper	25	Titanium	K_α	1790
25 μm molybdenum	30	Copper	K_α	3250
25 μm molybdenum	30	Lead	L_α	1160

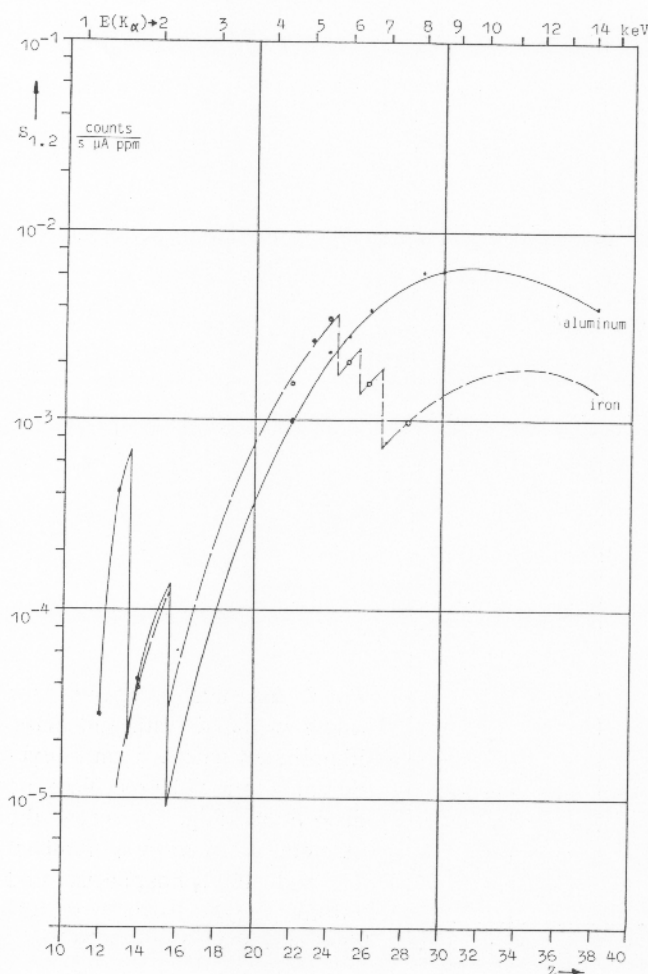

Fig. 9. Element intensities for traces in aluminum and iron. 5 μm molybdenum anode at 20 kV. Additionally to the discontinuity of the curves in Fig. 8 the X-ray absorption in aluminum respectively in iron generate further discontinuities

Trace Intensities in Glass, Aluminum, and Iron

According to the higher X-ray absorption in these materials the trace intensities are weaker compared to $S(Z)$ in epoxi. Moreover, the absorption in the main material and the fluorescence by the intensively X-radiating main material cause a more complicated curve of $S(Z)$. In the case of glass (Fig. 8) the intensity curve is only reduced, in the case of aluminum and iron (Fig. 9) additional absorption edges are to be recognized.

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