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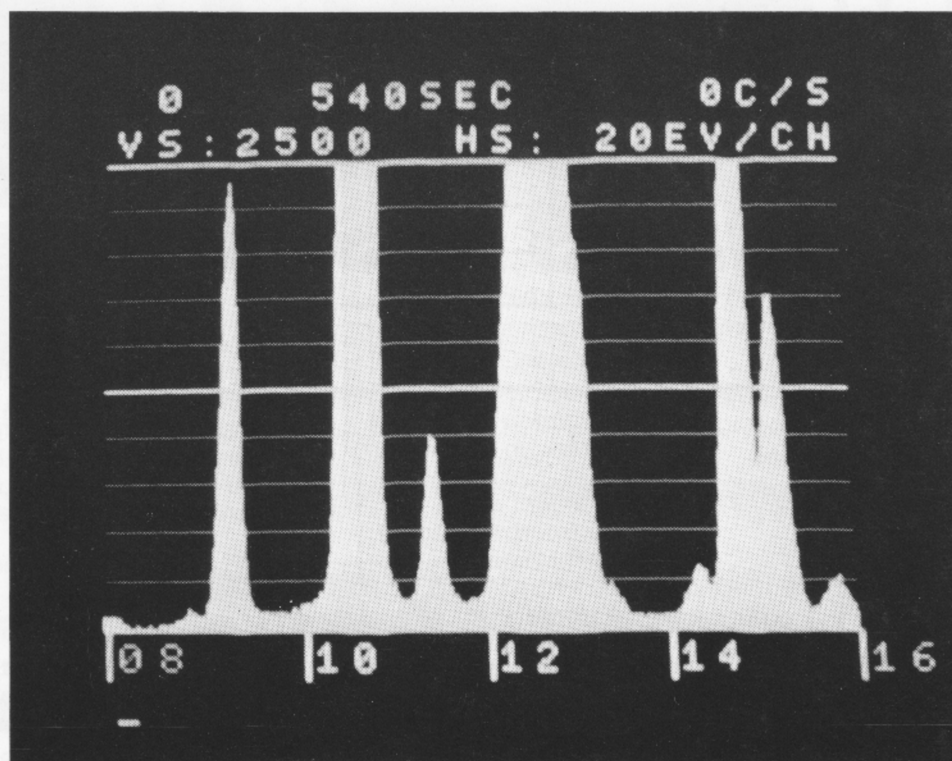
The Journal of Scanning Microscopy



Vol. 8, 5 (1986)
ISSN 0161-0457
Indexed in Current Contents

September/October 1986
FACM, Inc.
Mahwah, N. J., USA

SCANNING Vol. 8, 232–238 (1986)
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Received: June 4, 1986

Original Paper

X-Ray Fluorescence in the SEM – Advantages in Material Analysis

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1. Introduction

Usually, the electron beam is focused in the scanning electron microscope (SEM) onto the surface of the sample. While the excited secondary electrons generate the electron optical image, the x-rays excited at the point of impact enable an x-ray elemental analysis. Because of the short diffusion range of electrons in most non-biological materials, a high spatial resolution is achieved for material analysis, typically about 1 μm in all directions.

The benefits of this electron-excited x-ray analysis include the following:

1. Particle analysis: Particles of only 1 μm in diameter generate a clear x-ray signal.
2. Linescans and/or x-ray maps: Polished surfaces, especially cross-sections, are well suited for local analysis. The variation in concentration in one direction can be displayed as a linescan. Two-dimensionally, the elemental distribution can be presented as a map of bright dots, their density corresponding to the local concentration.
3. Quantitative analysis: Because of the small excitation depth of the order of the electron range, the intensity of the emitted x-rays is modified by absorption and fluorescence to a moderate degree only. Reasonable quantitative results can be obtained when using corrections for atomic number, absorption and fluorescence.
4. Light element analysis: Elements from boron to fluorine with only low-energy characteristic x-radiation can also be studied using wavelength-dispersive or window-less energy-dispersive spectrometers.
5. Information about surface coatings: Changing the energy of the primary electrons will modify their electron range. This allows the detection of variations in the composition of the material as a function of depth.

However, electron excited x-ray analysis is not well suited in other areas.

1. Trace analysis: The weak signals from elements of lower concentrations cannot be clearly detected in the x-ray spectrum because the continuous x-radiation overlaps the trace signals in the x-ray spectrum. Especially the widely used energy-dispersive spectrometers (EDS) with low energy resolution give spectra with a larger number of continuous x-ray quanta within the peak width of a characteristic x-ray line.
2. Analysis of insulating material: To prevent specimen charging, a carbon or metal coating is required, when the sample may be irreparably modified. Such a procedure will not be tolerable for unique specimens such as museum objects. Moreover, the characteristic x-radiation of a metal coating will be visible in the spectrum and some lines may overlap those due to the material.

3. Information about the depth of the material: Surface layers, such as electrolytically deposited coatings, for example, require cross-sectioning or at least abrasing of the layers. Both will destroy precious samples such as jewelry.
4. Analysis of medium Z material by K-lines: When the low-energy L-lines are overlapped, analysis using K-lines will often overcome the problem. However, the acceleration voltage of most SEMs is too restricted to excite these lines by higher electron energies.
5. Quantitative analysis of inhomogeneous material: Materials like solders, for example, tend to form eutectic crystals of variable composition. With an information depth of only 1 μm, the amount of material is too small for a really quantitative analysis.

These restrictions can be overcome by x-ray fluorescence analysis (XRF). This method is well proven in many areas of technology and science. An overview on XRF is given in the comprehensive book edited by *Herglotz* and *Birks* (1978). *Middleman* and *Geller* (1976) presented an XRF set-up inside an SEM so that the XRF method could be used in SEM analysis. *Linnemann* and *Reimer* (1978) compared the results of an experimental XRF set-up to direct electron beam excitation. Up to now, analysts report about minimum detectable concentrations of the order of 1 part per million (1ppm) (*Pozsgai* 1984, for example).

2. X-ray Fluorescence in the SEM

If an SEM-user mounts an x-ray source in the sample chamber, he can irradiate the sample with x-rays instead of bombarding it with high-energy electrons. He will observe the excitation of the characteristic x-radiation as before, but without the high continuous background (Bremsstrahlung) excited by the decelerating electrons. Such an x-ray source can be realized by using a small piece of metal as a bulk anode or by a thin metal sheet working as a foil anode. The impinging electrons of the primary electron beam will generate the characteristic x-radiation of the metal in this target. The user further needs a foil to prevent the reflected or scattered electrons from striking the sample, together with a small chamber to prevent the sample being irradiated by x-rays from the SEM polepiece or from the chamber walls.

The beginner has to consider two restrictions for the successful use of XRF in the SEM. At first, he has to use a sufficiently high electron beam current, if possible more than 1 μA. For this purpose, he should

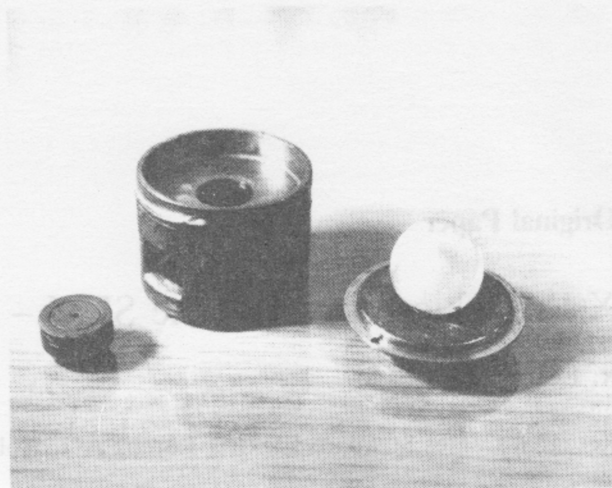

Fig. 1 The Roentgenbox. From left to right: Plug-in anode, cap, baseplate with sample, here an NBS test glass.

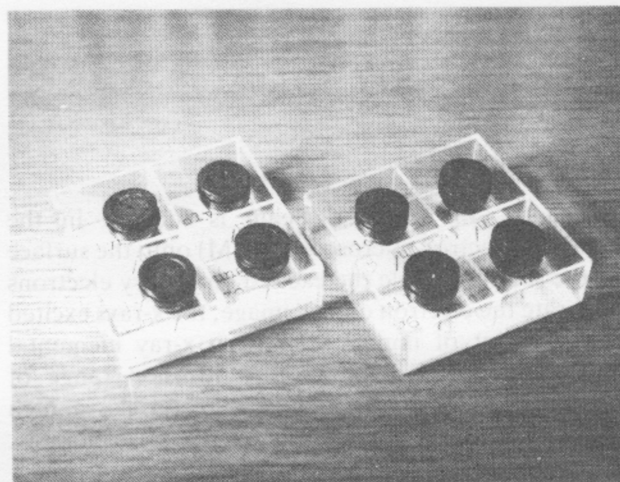

Fig. 2 Roentgenbox, set of plug-in anodes.

remove the aperture in the final polepiece and then switch to a larger spot size. It will be profitable to control the electron probe current by an electrometer. Additionally, the high voltage of the secondary electron detector has to be switched off to avoid damage by too many electrons. The second restriction consists in the geometrical alignment. The user has to make sure that the x-radiation from his sample will reach the x-ray detector. It is practical for the initial alignment to remove a side flange of the SEM chamber.

The tests described in the following were obtained using the XRF system "Roentgenbox" (*Eckert* 1982–1986, *Plannet* 1986). The Roentgenbox is equipped

with a set of different foil anodes for optimum excitation of the sample (see Figs. 1 and 2). Up to now, a number of analysts use it in the fields of material analysis and quality control.

As an example, Fig. 3 shows the spectrum of a sheet of lead. With electron excitation (Fig. 3a), a net peak height of Pb Lα of 9200 counts and the continuous background in this energy range of 800 counts gave a peak-to-background ratio of 11.5, with XRF in the SEM (Fig. 3b), the Pb L-lines are more intensively excited. In the same analysis time with the same counting rate, the peak height of Pb Lα was 50000 counts, but the background only 100 counts resulting in $P/B_{XRF} = 500$, more than 40 times larger than the P/B_{el} ratio of electron excitation. Now all lines of low peak intensity can be clearly seen (Fig. 3c).

3. Excitation of Medium Z K-lines

Elements with atomic numbers from Z = 40 to 56 (zirconium to barium) are often overlapped in their L-lines by lines of other elements, for example molybdenum with sulphur or barium with titanium and so on. Due to the difficulty of deconvolution, a low concentration of one component will introduce a large statistical error and falsify the quantitative result. When exciting the K-lines, an overlap will be avoided. Because of the different excitation laws, XRF shows better results. As an example, Fig. 4 shows the spectra of a tin foil with a small content of silver. The main line of silver (Ag Lα) is strongly overlapped by the tin line (Sn L_1), but there is no overlap in the K-lines. With electrons, an optimum excitation requires an electron energy E_{el} = 2 to 3 times E_{abs} (E_{abs} = energy of the absorption edge or ionisation energy of the excited shell). This means a high tension of about 60 kV, not achieved in most standard SEMs. In the case of XRF, x-rays with $E_x \geq E_{abs}$ will excite the material much more strongly when using an accelerating voltage of 30 kV.

4. Information about Deeper Layers

The electron bombardment of the sample surface informs the SEM user about a surface layer of the order of 1 μm in thickness. Deeper layers may deliver only negligible information about the composition of the material. Illuminating the sample with x-rays, these penetrate to a depth between 10 μm and 1 mm, depending on the material, the x-ray anode used and the SEM acceleration voltage. The information depth can become much larger and is only limited by the absorption of the exciting characteristic radiation in the material.

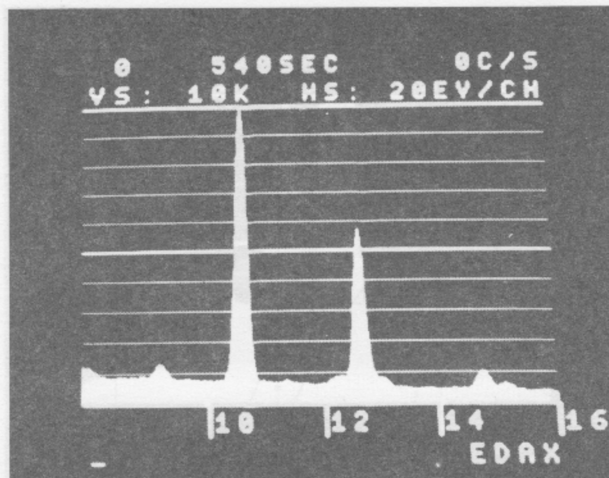

Fig. 3a

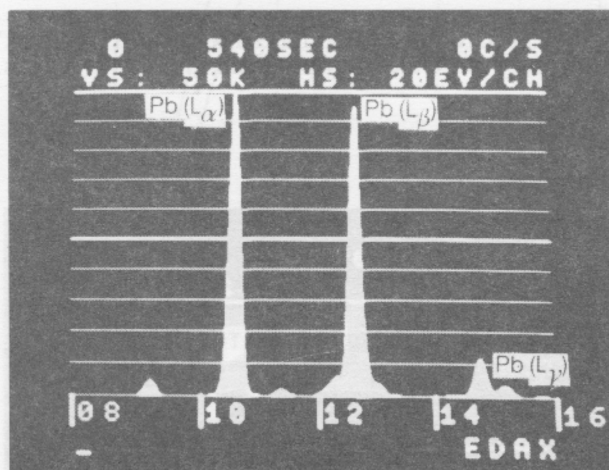

Fig. 3b

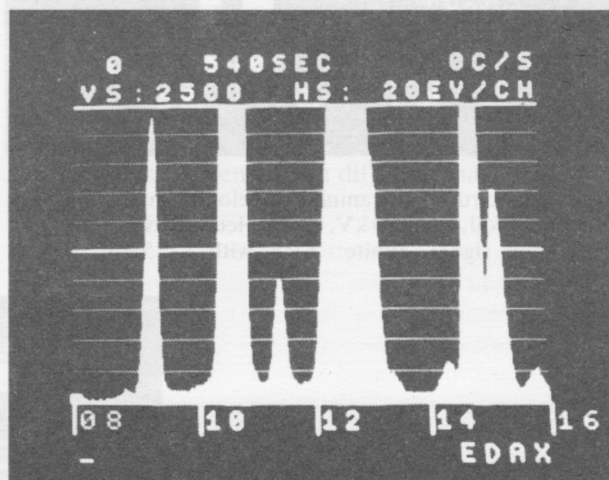

Fig. 3c

Fig. 3 Spectrum of lead using an accelerating voltage of 30 kV. (a) Electron excited; (b) XRF with a 50 μm thick molybdenum anode, vertical full scale: 50000 counts; (c) like (b), but vertical scale: 2500 counts.

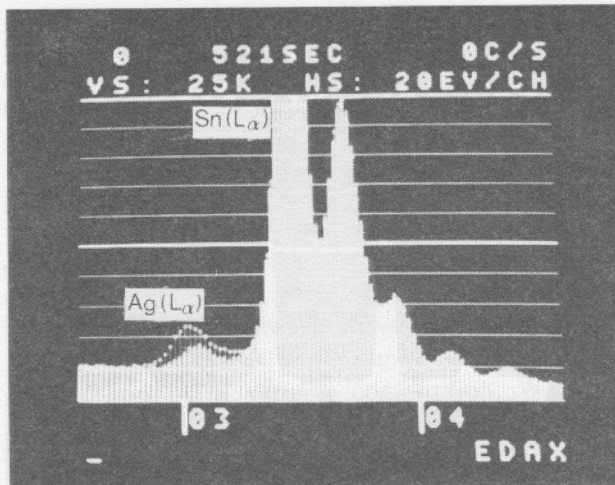

Fig. 4a

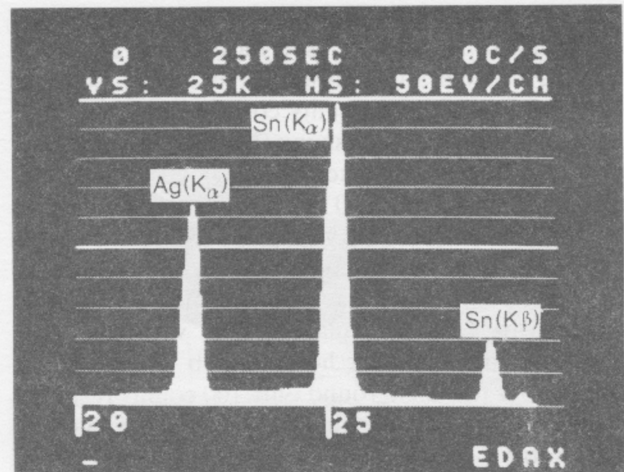

Fig. 4b

Fig. 4 Spectrum of a solder foil 3.5 Ag/96.5 Sn using 30 kV. (a) L-lines, electron excited. White: pure tin standard, gray: solder foil. Notice the overlap of both spectra. (b) K-lines, XRF with a 25 μm tungsten anode.

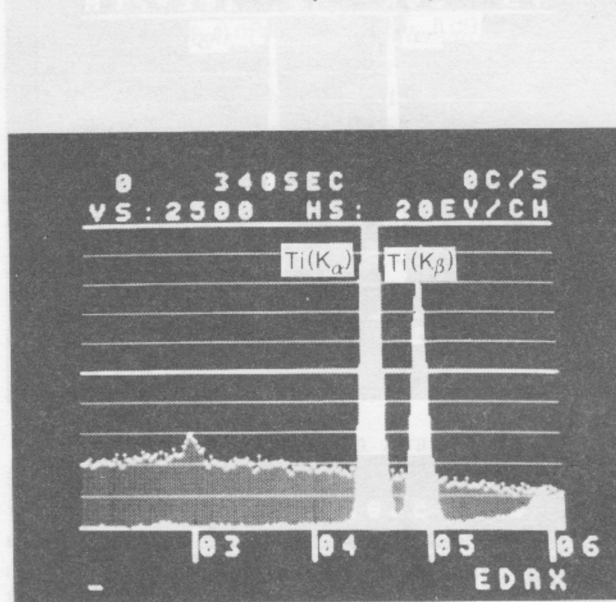

Fig. 5 Spectrum of titanium, enveloped in 40 μm thick aluminium foil, using 20 kV. Gray: electron excited without a titanium signal. White: XRF with a 25 μm copper anode.

Real bulk information is, therefore, available with XRF. Figure 5 demonstrates this with a sheet of titanium enveloped in a 40 μm aluminium foil. While the electrons do not penetrate the envelope, the titanium K-lines are clearly visible by XRF.

5. Information about Monocrystalline Areas

The XRF spectrum shows a strongly reduced background as compared with the electron excited spectrum because no Bremsstrahlung is generated. The XRF continuous spectrum stems mainly from the anode radiation scattered by the sample surface. However, this anode continuous radiation is Bremsstrahlung excited on top of the foil anode and filtered by the bottom material of the foil. This continuous radiation will only be weakly scattered by the sample. On the other hand, when the sample contains monocrystalline areas, all x-ray quanta which fulfil Bragg's law

$$n \lambda = 2 d \cos \Theta, \quad \lambda = h c / E_x \tag{1}$$

can be Bragg reflected with high intensity. The background of the spectrum is modulated with a number of sharp peaks which are not correlated to elemental x-ray lines. Because of the angle 2 Θ between the incident x-rays from the foil anode and the detector direction, changing the orientation of the reflecting specimen will also change the energy of these lines in the spectrum. Figure 6 represents the spectrum of a monocrystalline silicon wafer illuminated with the continuous spectrum from the anode. The Bragg peaks are clearly visible. Though a specimen will not often contain such large monocrystalline areas, XRF in the SEM can give information about the crystalline state by using these peaks.

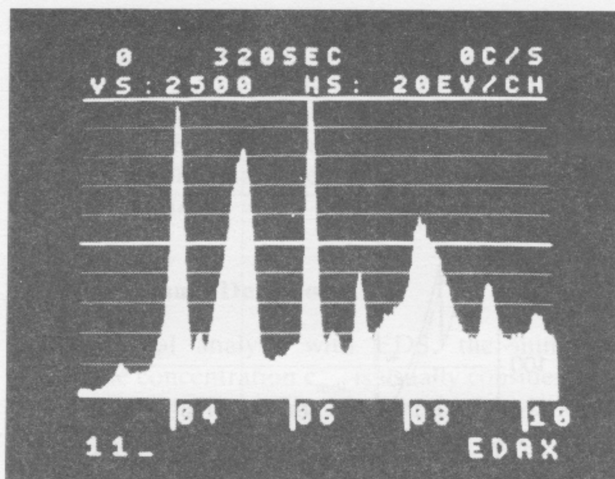

Fig. 6 Spectrum of a monocrystalline silicon wafer. XRF with a 7 µm aluminium anode using 20 kV. The lines are caused by Bragg reflections of the continuous x-rays from the anode.

6. Trace Analysis

As mentioned in the introduction, trace analysis is a main field of application of XRF in the SEM. The low background of the spectrum in one reason. The other reason is the possibility of intensively exciting the lines of trace elements in one part of the spectrum, whilst exciting the lines of the main elements in another energy range to a moderate intensity only. Therefore, the limited counting rate of the EDS system of the order of 2000 counts per second (cps), is mostly sufficient for analysing the trace elements.

Figure 7 represents the spectrum of an aluminium alloy with 90% aluminium and only 0.6‰ strontium. The strontium peak Sr Kα is higher than the aluminium peak Al K: The exciting x-ray radiation from the anode, mainly the molybdenum K-lines at 17.4 and 19.6 keV can excite lines of elements in the 8 to 15 keV range with high intensity, but lines of elements as aluminium with E_{abs} = 1.56 keV only with low intensity. Here a titanium anode with Ti K = 4.51 keV will result in higher intensities. These qualitative statements are verified quantitatively in Figs. 8 and 9. Here the signal net intensities S were measured for a number of trace elements in different materials using the relation

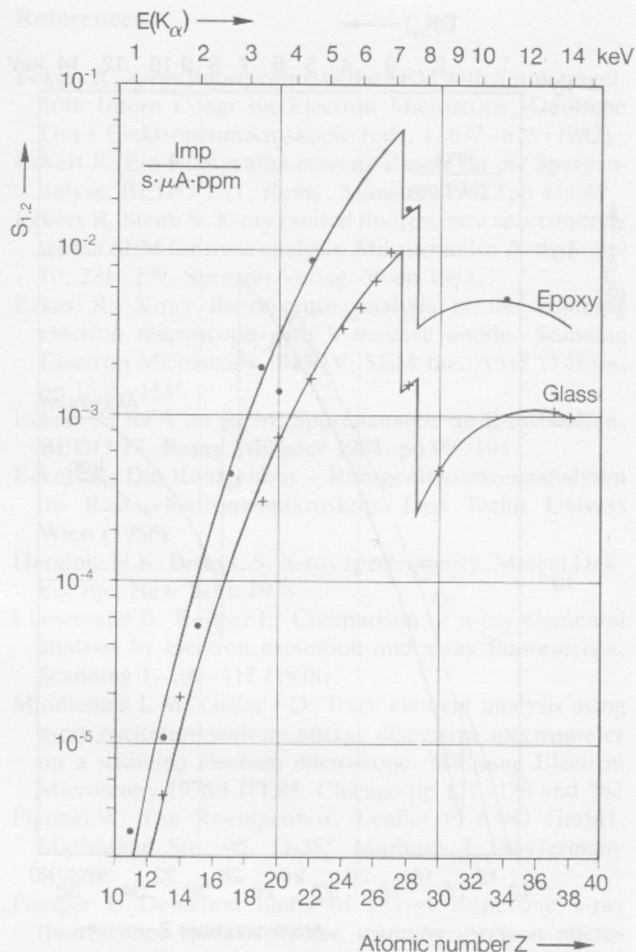

Fig. 8 Signal intensities of traces in epoxy and glass. XRF with a 25 µm copper anode using 20 kV.

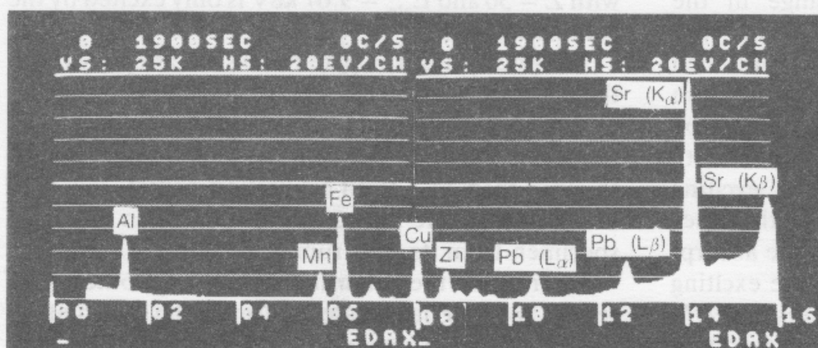

Fig. 7 Spectrum of an aluminium standard with 0.06% strontium. XRF with a 50 µm molybdenum anode using 30 kV.

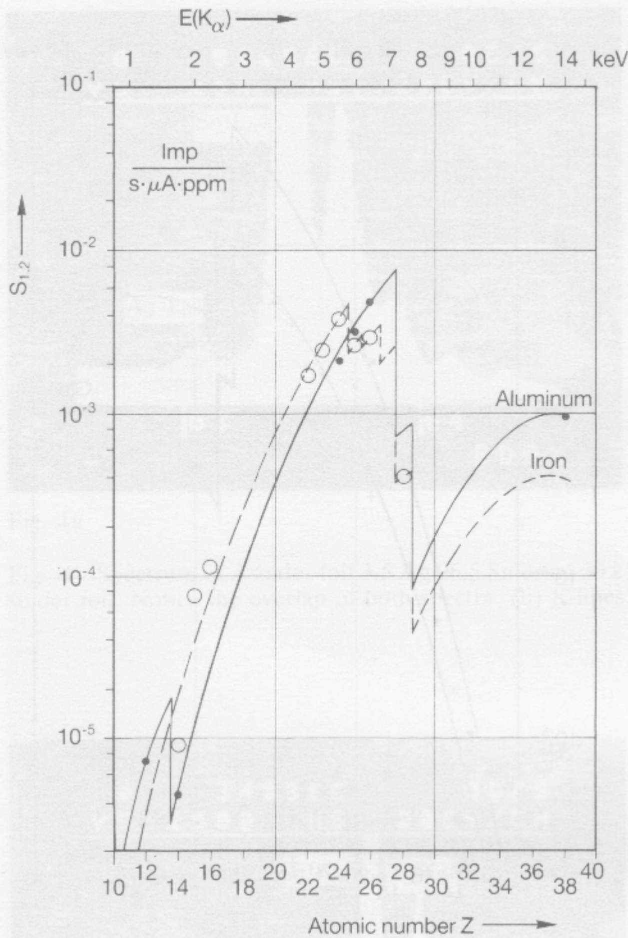

Fig. 9 Signal intensities of trace elements in aluminium and iron. XRF with a 25 μm copper anode using 20 kV.

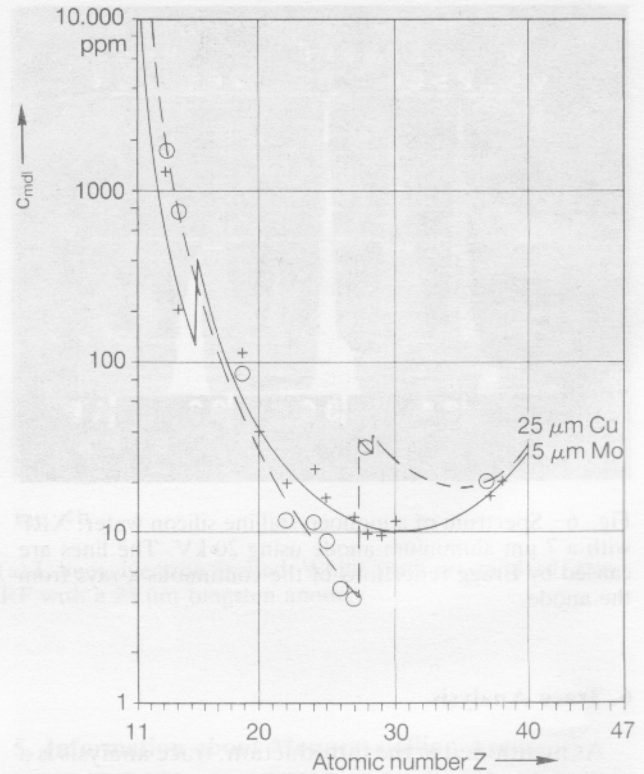

Fig. 10 Minimum detectable concentrations of trace elements in glass. XRF using 20 kV with a 25 μm copper anode and a 5 μm molybdenum anode, 2000 c. p. s., counting time 1000 s.

$$S = \frac{N}{t\ I\ c} \qquad (2)$$

where N = net number of x-ray counts, t = counting time, I = electron beam current and c = concentration of the trace element. The energy range in the spectrum was choosen close to 1.2 × FWHM (full width at half maximum), say 140 to 220 eV and then extrapolated to the exact 1.2 FWHM. This procedure mostly acquires a small correction only. As can be seen by the curves, the intensities decrease with increasing energy difference between the exciting anode line and the absorption energy of the trace elements. Steps in the curves occur when the absorption energy is higher than the energy of the exciting lines. For example, cobalt with Z = 27 and E_{abs} = 7.71 keV will be excited strongly when using a copper anode with Cu Kα = 8.04 and Cu Kβ = 8.90 keV. In contrast, nickel with Z = 28 and E_{abs} = 8.34 keV can be excited by the weak Cu Kβ-line, together with the continuous anode radiation with E_x > 8.34 keV. Zinc with Z = 30 and E_{abs} = 9.67 keV is only excited by the continuum with E_x > 9.67 keV.

In a poorly absorbing material such as epoxy resin, the net trace signal will increase linearly with concentration up to about 1 per thousand. In a more highly absorbing material like iron, the linear range extends to more than 1%. With calibration curves, the XRF user can calculate the concentrations of an unknown specimen from its spectrum.

To transfer the intensity curves to another XRF set-up, the user has first to determine the sensitivity of his set-up. For example, the curves in the figure were

measured with an equipment where an iron sheet of 1 cm^2 illuminated by the radiation of a 25 μm copper anode at 20 keV, producing a net intensity of $S_{Fe} = 2.9 \times 10^{-3}$ counts/s μA ppm with an energy window $\triangle E$ = 180 eV of the EDS. The intensities can be transferred from one set-up to another by being multiplied by a sensitivity factor.

7. The Minimum Detection Limit

In material analysis with EDS, the minimum detectable concentration c_{mdl} is usually considered to generate a signal three times the standard deviation of the background. With N_B counts in the background, we get

$$c_{mdl} = 3\ a\ N_B^{1/2} \quad (3)$$

Therefore, the detection limit c_{mdl} can be extrapolated from a measured spectrum by

$$c_o = a\ N \quad (4)$$

Figure 10 represents c_{mdl} values of trace elements in glass. Compared with electron excitation, the detection limit with XRF in the SEM is mostly 10 to 100 times lower.

where $a = 1/S\,t\,I$. According to eq. (2), a material with the certified concentration c_o generates a net signal N, so that

$$c_{mdl} = \frac{3\ N_B^{1/2}}{N}\ c_o \quad (5)$$

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