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X-Ray Excited Fluorescence Spectroscopy Within SEM for Trace Analysis

By

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With 6 Figures

(Received January 19, 1983)

1. Methodical Fundamentals

1.1 Electron Excited Radiation

Within the scanning electron microscope (SEM) the electron beam scans line by line across the sample. The reflected electrons which emerge from the primary beam and the secondary electrons which are knocked out of the surface of the sample are used to produce the electron optical picture. The X-rays generated at the corresponding points of electron impact enable a chemical analysis of the surface of the sample within a depth of information of about 1 μm. The positionable fine electron beam with its diameter of nearly 0.1 μm produces a clear X-ray signal on particles of 1 μm, e.g. 10^{-12} g. More limited is the detectability of uniformly spread material traces, as alloy ingredients. Here the Bremsstrahlung, generated by the stopping of primary electrons hides in its statistical fluctuations the weak signals of trace elements. This is the case especially for energy dispersive spectrometers with their relatively poor energy dispersion, as they are commonly used at the SEM.

1.2 X-Ray Excited Radiation

Illuminating the sample with X-rays will generate characteristic radiation without generation of Bremsstrahlung. Therefore in trace analysis X-ray

fluorescence is widely used. Accordingly SEM-workers try to adapt the methods of X-ray fluorescence on their instruments.

2. Experimental Fundamentals

2.1 X-Ray Source with a Foil Anode

The hitherto proposed and used constructions[1-5] adapt the X-ray transmission tube to the SEM, see Fig. 1. The electron beam hits a thin metal foil and
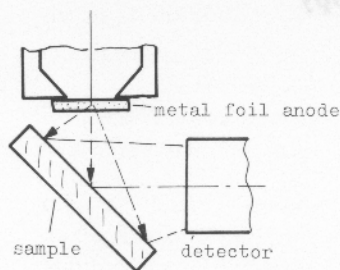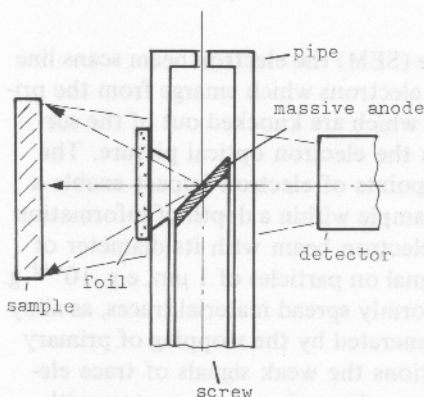

Fig. 1. Foil anode

Fig. 2. Massive anode

generates in the upper 1-μm-slice X-radiation. The X-rays penetrate the remaining foil and illuminate the sample. An advantage of the construction is the high intensity of the X-ray beam produced by a moderate electron current. In addition to this the foil acts as an X-ray filter. With suitable choice of the material and of the thickness of the foil this anode yields

nearly monoenergetic radiation which irradiates the sample. A certain problem arises by the fact that usually only part of the primary electrons is absorbed and excites X-rays and that another part of the primary electrons transmits the foil. Especially for the detection of elements with low atomic number, i.e. in the low energy range of the spectrum ($E < 4$ keV) problems arise by the transmitted electrons which produce Bremsstrahlung on the sample, which hinders the detection of trace elements. Using a foil thick enough for 100 % absorption of the primary electrons yields only highly energetic X-rays which are inconvenient for the excitation of light elements ($Z \leqslant 14$). Nevertheless the constructions with an anode foil yield finally an X-ray spectrum from the specimen with markedly reduced background compared to an electron-excited spectrum. To the time, at least one construction is used commercially[6].

2.2 X-Ray Source with a Massive Anode

In the following an X-ray source for the SEM is presented which is equivalent to the usual X-ray tube using a massive target (Fig. 2). In this construction the electron beam incidents from the electron optical column onto the anode, which is formed by a small (4×3 mm^2) metal sheet of about 1 mm thickness. The anode is placed within a pipe with a small opening on the top and a larger opening at the side for the emerging of the generated X-rays. The window at the side is closed with a thin foil for the absorption of scattered electrons. Thereby the set up corresponds to the usual equipment for X-ray fluorescence analysis. Most of the facilities needed for performing this kind of analysis are contained within a commercial SEM-equipment, namely an electron source with $V = 0$ to 40 kV, $I = 0$ to 10 μA; a vacuum equipment for pressures down to 10^{-5} mbar; a vacuum chamber with mechanical controls for the sample, and an energy dispersive spectrometer with analysis system.

In the present construction[7,8] the anode sheet metal is sticked onto the top of a screw. The pipe with the foil window (that means the whole filter) is slipped on the screw. It works as Faraday cage. Anode and filter can be changed without problems. The anode is screwed into a plate together with a movable sample holder. To protect the sample from electrons and X-rays scattered from the walls of the vacuum chamber of the SEM the whole arrangement consisting of pipe and sample is surrounded by a metal enclosure which contains in the center of its upper side a small hole for the incoming electron beam. Furthermore this enclosure contains in its side wall directed to the spectrometer (Si(Li)-detector) a larger opening for the X-rays emerging from the sample.

The ground plate is screwed onto an usual sample holder of the SEM. Thus the switching over from the usual examinations in the SEM to a trace analy-

sis in the ppm-range reduces to a changing of a sample holder only. All electrical conducting and vacuum resistent materials may be used as construction material for the anodes, i.e. nearly all metals. Since the electrical power dissipation is limited almost to about 0.1 W, different from usual X-ray tubes even brittle materials such as silicon may be used. Also the filter foils with their area of about 1 cm² may be used in a large variety since there is no atmospheric pressure difference on their surface. Corresponding to this fact the mechanical strength is not the limiting factor. The user of a SEM has for his investigations with the X-ray source the benefits of better use of the existing equipment and of good adaption to the analysis conditions with a wide range of selection of anode- and filter-materials.

Certain limitations result by limited sample size (area 0.1 to 5 cm², thickness up to 1 cm), vacuum resistance of the sample, and poor counting rates for a beam current < 1 μA.

2.2.1 Peak to Background Ratio

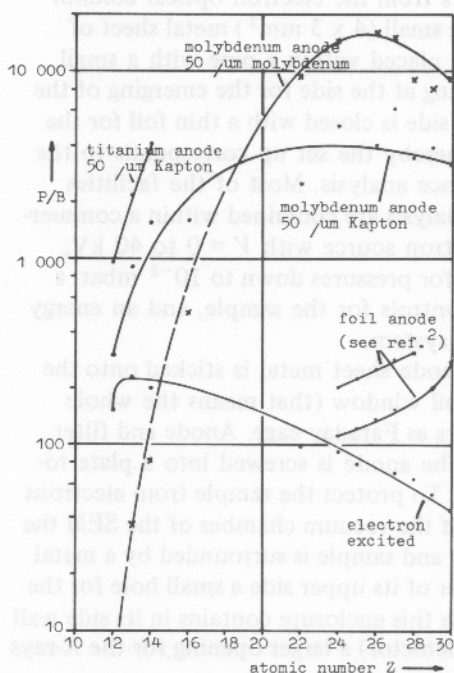The ratio of the X-ray net signal peak to the background (P/B) serves as a

Fig. 3. P/B-ratio versus atomic number Z for the K-emission lines of elements. Primary electron acceleration voltage V = 20 kV

scale for the achieved decrease of the X-ray background. For example, with electron excitation pure elements exhibit P/B = 20 to 200, depending on the element, the beam voltage, and the take off angle of the radiation. Constructions with foil anodes reach up to P/B = 100 to 300 for elements with an atomic number $Z > 20$. The presented X-ray source produces for elements with $Z = 12$ to 16 a P/B = 1000 to 3000 and for elements with $Z > 16$ a P/B = 3000 to 15000, see Fig. 3. Thus the enhancement compared to electron excitation amounts for elements with $Z \leqslant 16$ to about 10 times and for $Z > 16$ to about 20 to 200 times.

The achieved P/B-ratio depends on the element and the impinging X-radiation.

2.2.2 Filtering

Concerning the choice of the filter material, the following facts should be observed.

A thin plastic filter foil absorbs the reflected electrons from the anode but transmits nearly the entire anode X-radiation. This radiation will generate the fluorescence radiation of the sample, but is also scattered by the sample and superimposes on the desired fluorescence spectrum. Thus a complex photon spectrum finally reaches the detector and causes a nearly constant ratio peak to background of about P/B = 3000 over a wide range of elements with satisfactory count rates. However, in the case of crystalline samples, the sample X-ray spectrum in addition contains also strong Bragg-reflexions (see Fig. 4). These reflexions may overlap sometimes with the signals of the trace elements to be detected. Given a certain angle 2θ between the direction of the primary beam and the connection line between specimen and detector only X-rays with quantum energy $E = \frac{nhc}{2d\sin\theta}$ are reflected by net planes with distance d into the detector. With single crystalline material or with coarse grained material there is a chance to diminish the intensity of the reflected beam by turning the specimen.
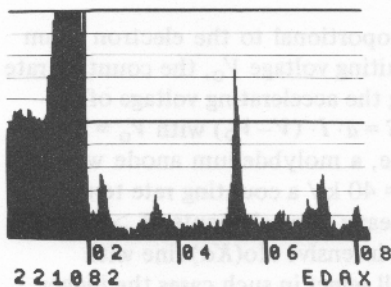

Fig. 4. Silicon spectrum; Ti-anode; 7.5-μm Kaptonfilter

With a higher absorbing metal filter foil the high energy part of the anode spectrum reaches the sample, whereas the low energy part is absorbed in the foil. Therefore the sample spectrum stays free from reflected low energy X-rays. With such a filtered X-ray excitation for elements with $Z = 24$ to 40 a ratio peak to background of about $P/B = 10000$ up to 15000 is reached. Thus P/B is three to four times larger than with unfiltered excitation. However, the larger P/B values which can be achieved using filtered excitation are only valid for elements with absorption energies not too far from the excitation energy. The curves $P/B = f(Z)$ are steeper than with unfiltered radiation (see Fig. 3).

Furthermore, the low background is obtained only in the high energy part of the peak, which corresponds in Fig. 5 to the right hand side. In this region the signal reaches 50440 and the background 3 thus yielding $P/B = 16800$. In the low energy range on the left hand side of the peak the background is enlarged as a result of a minor absorption of the sample radiation in the material together with Compton scattering, i.e. inelastic scattering of the X-radiation in the sample and the detector[9]. This is to be considered for doing trace analysis.
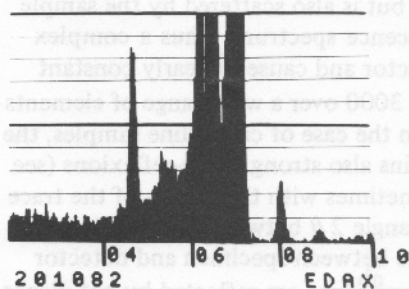
Fig. 5. Iron spectrum; Mo-anode; 50-μm Molybdenumfilter

2.2.3 Counting Rate

The counting rate S in the detector is proportional to the electron beam current I. Furthermore, after passing a limiting voltage V_0, the counting rate is nearly proportional to $(V-V_0)$, V being the accelerating voltage of the electron beam. Thus the relation stands: $S = a \cdot I \cdot (V-V_0)$ with $V_0 = $ const.; $a = $ proportionality factor. As an example, a molybdenum anode with a 50 μm-molybdenum filter produces at $V = 40$ kV a counting rate ten times higher than at $V = 20$ kV. Furthermore, heavy trace elements ($Z > 30$) in a light matrix are effectively excited by the intensive Mo($K\alpha$) line with 17.5 keV. Therefore the user of a SEM will select in such cases the higher beam voltage region. Since a number of SEM's have a high voltage limit of

20 to 25 kV, both examples in chapter 3.2 were measured with a beam voltage of only 20 kV.

3. Application of the X-Ray Source with Massive Anode to Trace Analysis

3.1 Strategy in Trace Analysis

If there is a sample with unknown traces one should use as a first step the unfiltered excitation. As the second step, to compare the traces with the contents in a standard, the filtered excitation should be applied, using such a radiation energy, that only the traces are excited and not the major elements. In this way a larger part of the counting rate (usually about 2000 counts per second = cps) falls into the energy interval of the trace, see Fig. 6. The anode material should be chosen in such a way that the region in the energy scale showing the highest intensity lies only a small amount higher than the absorbing energy E_{abs} of the element to be detected. In addition for the case $E_{abs\ trace} < E_{abs\ matrix}$ the energy of the anode radiation should be chosen lower than $E_{abs\ matrix}$ (compare with lower part of Fig. 6).
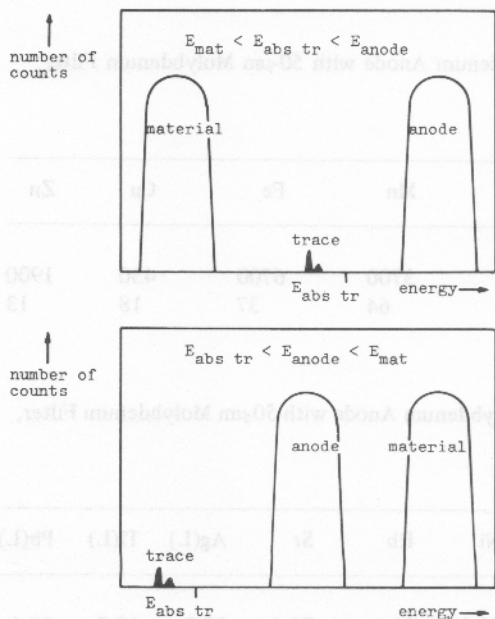

Fig. 6. Schematic diagram for the choice of the primary X-radiation in trace analysis

3.2 Detectable Minimum Concentration

For the present paper the following definition for the detectable minimum concentration c_{min} was used (see, for example[9]):

$$c_{min} = \frac{3\sqrt{N_B} \cdot c_0}{(N - N_B)}$$

with N_B = number of background counts

N = total number of counts of a characteristic line of a reference element

c_0 = concentration of the reference element

Hereby is assumed, that c_{min} corresponds to three times the standard deviation of the background in a certain energy interval ΔE. The energy interval is assumed to be 1.2 times the full width at half maximum (FWHM).

Two materials were analysed for evaluating the detection limits: an aluminum standard with a number of trace elements in the 2000 ppm range and the NBS glass 612 with traces in the 50-ppm range. For both standards the same measurement conditions were applied. The results are listed in Table 1 and Table 2.

Table 1. Aluminum Standard, Molybdenum Anode with 50-μm Molybdenum Filter, 20 kV, Counting Time 20 min

Trace	Ti	Cr	Mn	Fe	Cu	Zn
c_0 [ppm]	530	1800	3700	6700	430	1900
c_{min} [ppm]	1310	59	64	37	18	13

Table 2. Glass Standard NBS 612, Molybdenum Anode with 50-μm Molybdenum Filter, 20 kV, Counting Time 20 min.

Trace	Ca	Fe	Ni	Rb	Sr	Ag(L)	Tl(L)	Pb(L)
c_0 [ppm]	86000	51	38.8	31.4	78.4	22.0	15.7	38.6
c_{min} [ppm]	110	3.8	4.1	8.8	14	50	7.0	3.2

Summary

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Since the excitation of X-ray fluorescence by primary X-rays shows advantages compared to primary electrons, also for the use in a SEM an X-ray excited fluorescence attachment is proposed. This works with massive anode which shows advantages compared to the well known foil anode method. This X-ray source with a massive anode permits the performance of trace analyses in the SEM. Apart from an additional use of the existing equipment a large variety of anodes and filters enables the user to adapt the measurement conditions to the analysis problem. P/B-ratios of mostly 3000 to 15000 in pure elements are usual with this method and therefore detectable concentrations in the ppm range are secured.

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