Plastic material often contains Cadmium oxide as a colour pigment. The Cadmium contents of various specimens may be measured e.g. by atomic absorption spectroscopy (as in this example) or by chemical analysis. These specimens are then also investigated by SEMRAY XRF analysis. As a result a calibration diagram as shown in Fig. 8 may be obtained. This curve shows the peak area of the Cadmium peak versus the Cadmium contents. The Cadmium contents of an unknown specimen may easily be obtained by measuring the Cadmium peak area and subsequent use of the calibration diagram.

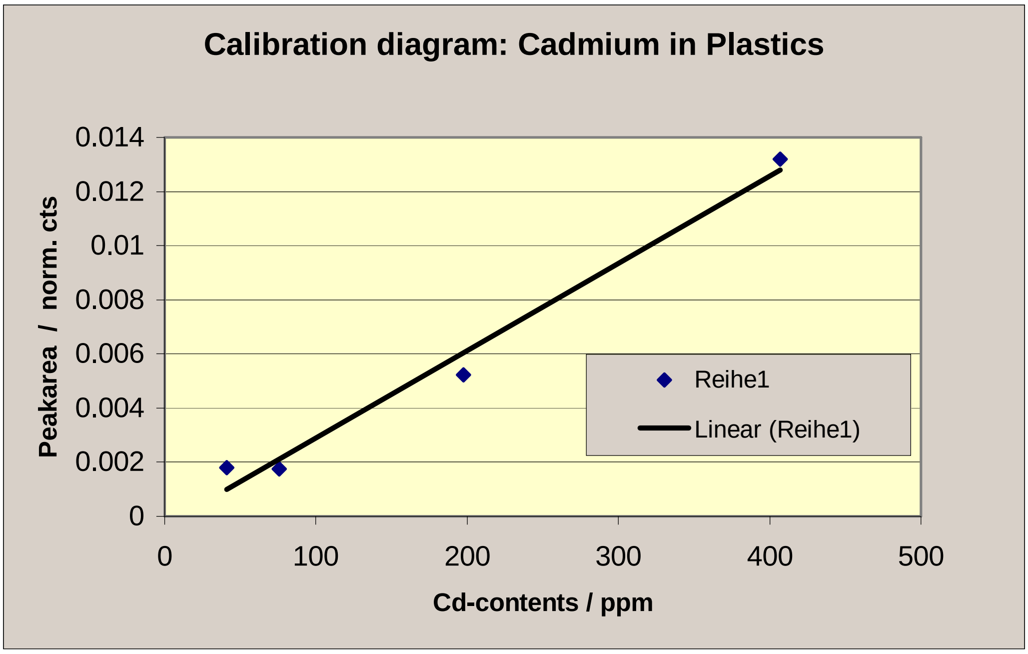

Fig.8
Calibration diagram for the quantitative analysis of Cd in a plastic material

Conclusions

SEMRAY XRF measurements in combination with an existing EDS system turn out to be a most powerful tool to extend the analysing properties of the SEM into the ppm range. Even bulk analysis through surface layers are possible. Strong points of the system are :

- Detection limit in the range of some ten ppm
- X-radiation is characterized by a larger depth of penetration as compared to an electron beam; consequently, SEMRAY spectra enable bulk analyses.
- With X-ray excitation, also sensitive samples can be investigated, which would be destroyed under direct electron bombardment (e.g. biological specimen).
- Sputtering of samples against charge phenomena is not required for X-ray probe XRF-analysis. This means less time involved, as well as preservation of the sample in its intact original state (important e.g. for precious samples).
- no specific demands on the condition of the sample surface (investigation of rough or open-structured specimen).
- The method employed by the SEMRAY-system provides a quality of analysis according to that of standard XRF at a low fraction of the costs of an XRF-instrument.

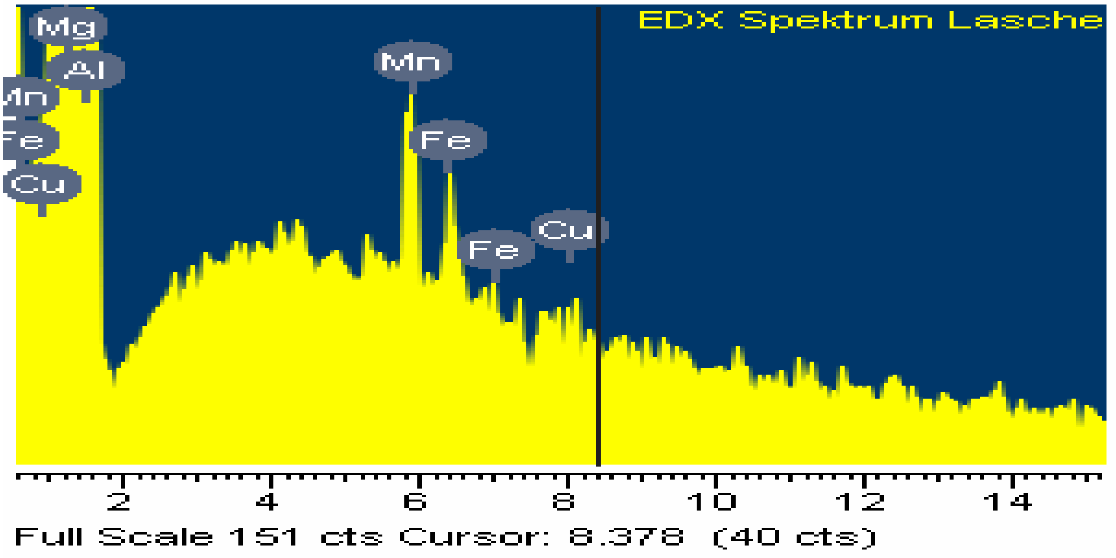

Fig.7a EDS spectrum of a beverage can clip showing Al and some alloy elements (20 kV)

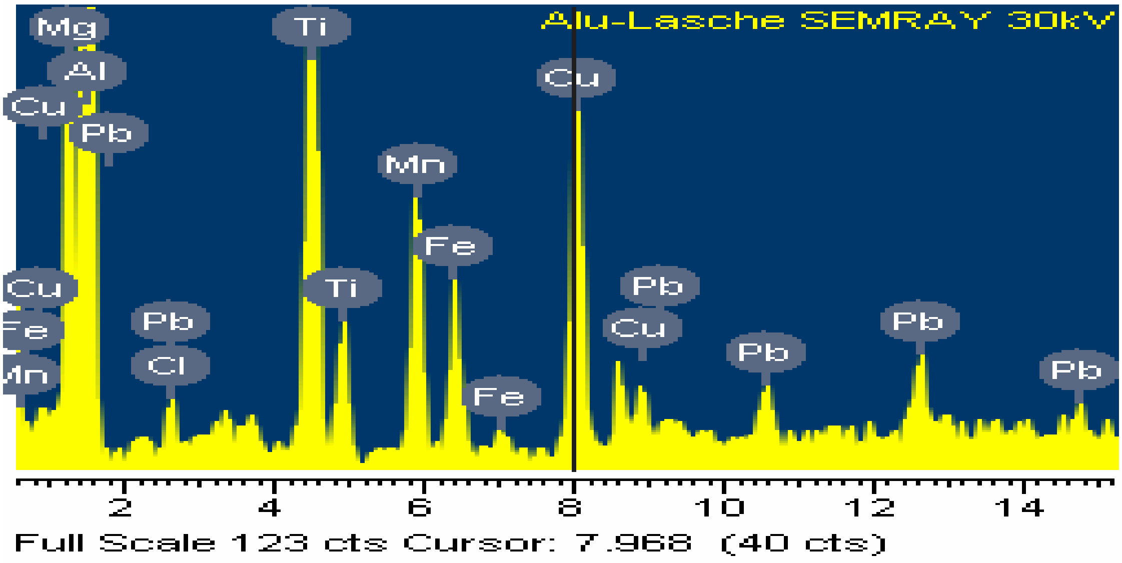

Fig.7b SEMRAY XRF spectrum of a beverage can clip showing a lead impurity (Ti target)

5. Quantitative XRF Analysis

A frequently asked question concerns the possibility of standardless quantitative analyses by XRF. In most EDS systems there are no algorithms included enabling the standardless calculation of quantitative results from XRF spectra. Main reason for this situation is the different interaction between electrons and material or X-rays and material. Compared to electron beam induced X-radiation, X-ray induced X-Ray radiation is created in different penetration depths, undergoes different absorption phenomena and does not create any Bremsstrahlung. But quantitative algorithms included in an EDS analyser are just optimised for electron beam induced X-ray radiation.

Therefore, a most valid alternative is the quantitative analysis by using standards, as is also done during WDS X-ray analyses. Fig. 8 shows a suited example.

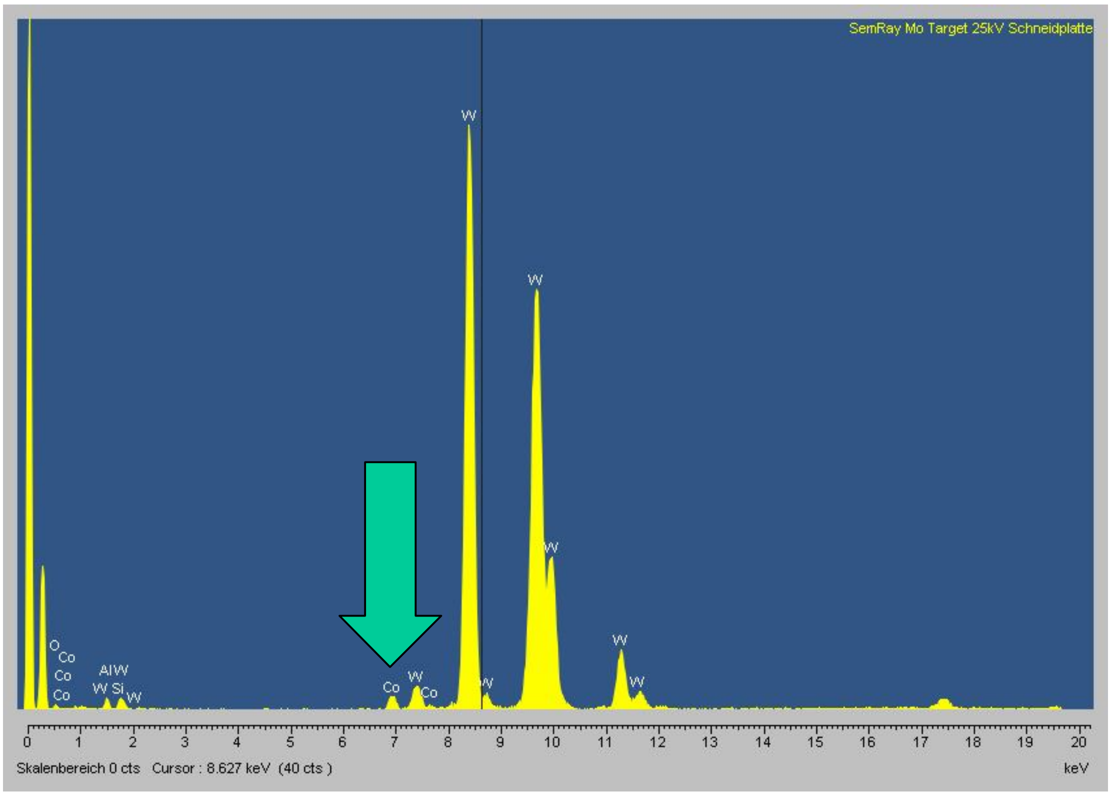

Fig.6b
SEMRAY XRF spectrum of a diamond coated hard metal (W:Co) machine tool (Mo-target). Green arrow indicates the Cobalt peak

4. Beverage Can Clip

In the present case the clips of a beverage can were teared off, but the can was not opened. One possibility for this undesired behaviour is the composition of the material the pin is made of. Fig. 7a shows the EDS spectrum of the pin. Only Aluminium and the two alloy elements Iron and Copper occur. Obviously, this gives no advice for the origin of the tear-off phenomenon. However, the Semray XRF spectrum (Fig. 7b) shows the presence of Lead in trace concentrations. It is known that the mechanical strength of Aluminium alloys becomes less if small amounts of Lead are present. Apparently the SEMRAY investigation is uniquely suited to solve this quality problem.

Fig. 5a shows the EDS spectrum of a $BaTiO_3$ ceramic doped with 0.03 % Yttrium (30 ppm). The elemental components show their individual spectral lines. Y is missing because its concentration is well below the EDS detection limit. The Semray XRF spectrum in fig.5b does not only show the Y-peak, but also indicates that there also a certain amount of Sr is present in the ceramic. This is well known because Barium can not be seperated exactly from Strontium during the production process.

3. Hard metal machine tools

For better stableness, hard metal (W:Co) machine tools like drillers or cutting tools are coated with diamond layers with thicknesses in the range of 5 - 10 µm. Unfortunately, a good adhesion of the diamond layers requires the presence of Co in the interface region. Co occurs in the bulk material in small concentrations as a sintering aid, but often it is depleted on the surface. In these cases the diamond layers are flaking off. In order to investigate such phenomena by EDS the specimens have to be delayered because the electron beam may not penetrate the diamond layer. Delayering a complicated structure like a driller is not economic.

EDS spectra of an diamond coated machine tool show regularly only a strong Carbon peak (Fig. 6a) and do not contribute to a solution. SEMRAY XRF investigations, however, look 'through' the diamond layer and clearly show the hard metal matrix. Even the Co peak can be found unambiguously. Therefore the quality control can be performed without difficulties.

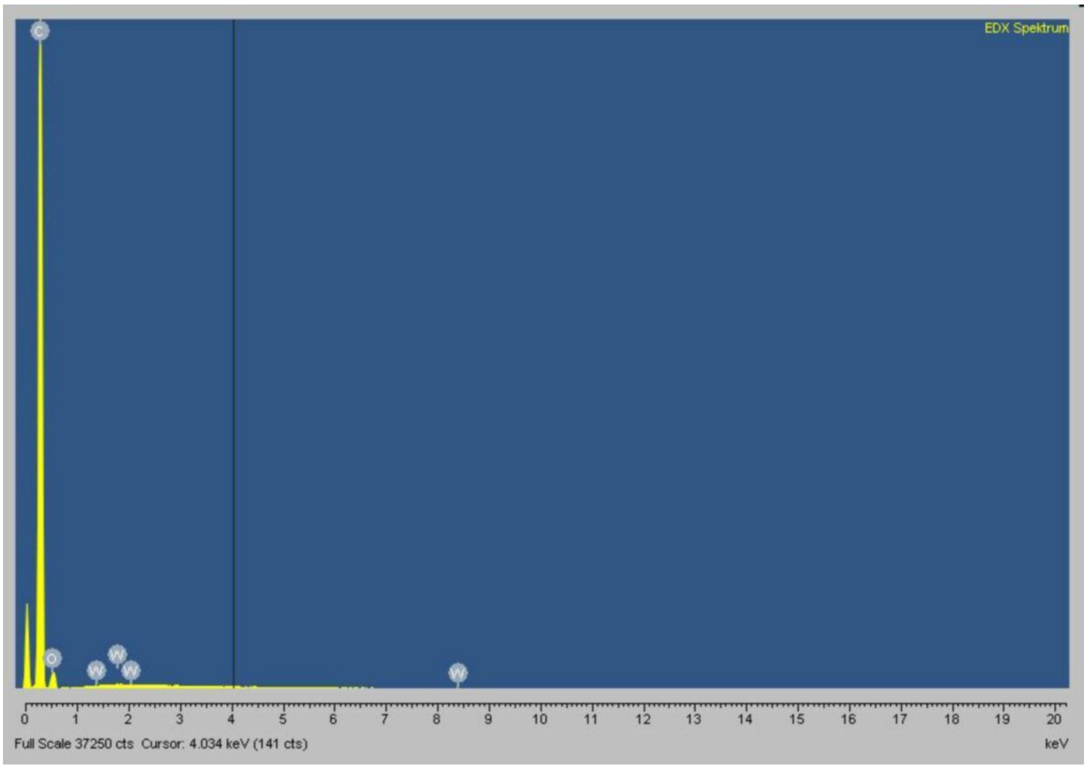

Fig.6a
EDS spectrum of a diamond coated hard metal (W:Co) machine tool (20 kV)

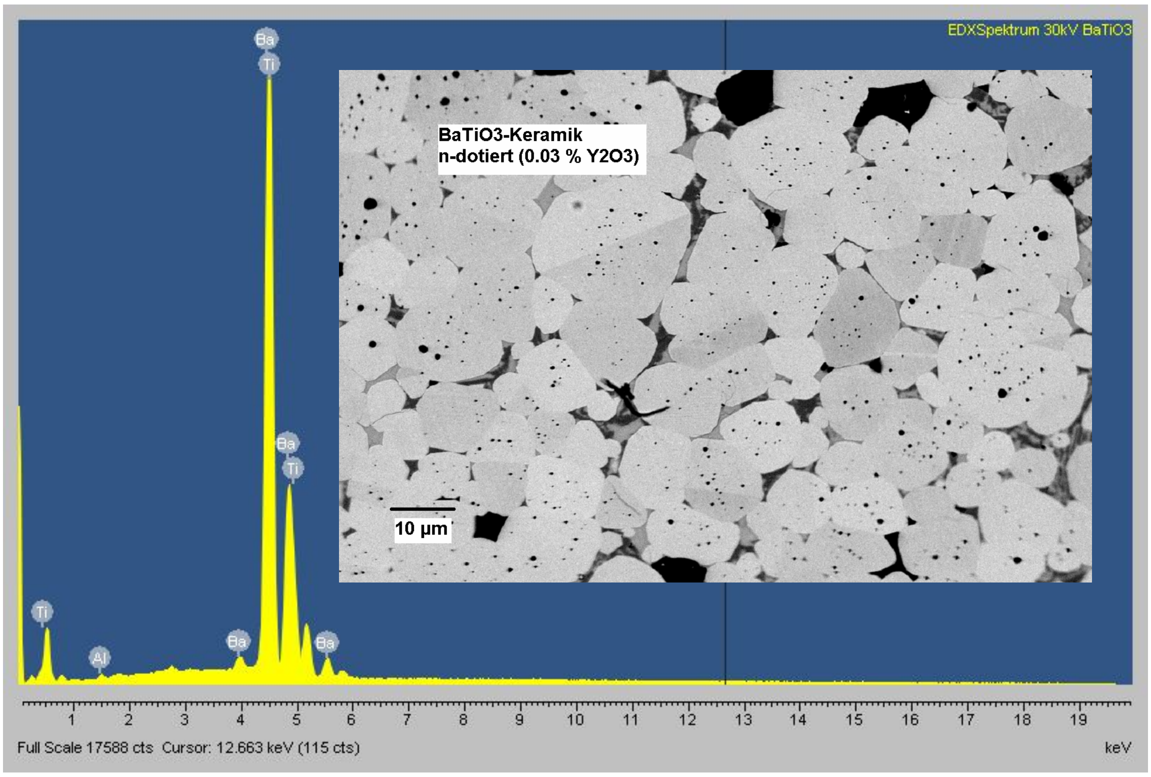

Fig.5a
EDS spectrum of a Yttrium-doped Bariumtitanate Ceramic (20 kV). Inserted BSE-image showing the grain structure of the sintered ceramic

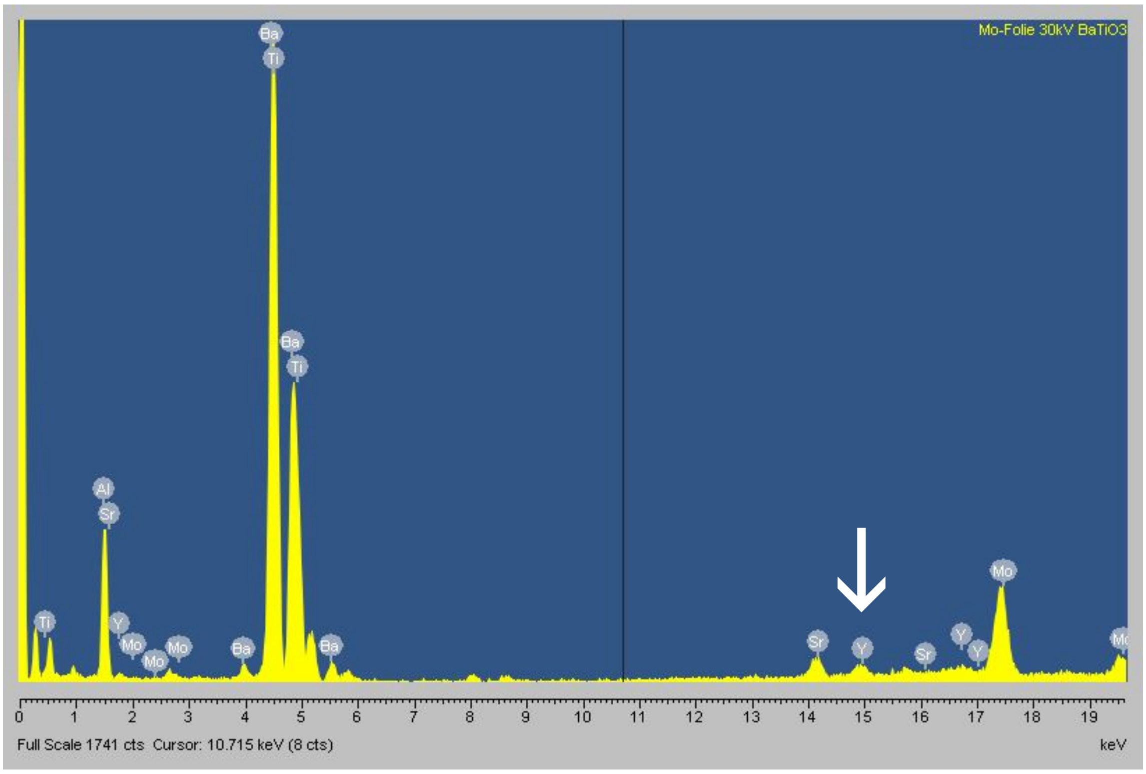

Fig.5b
SEMRAY XRF spectrum of a Yttrium-doped Bariumtitanate Ceramic (Mo-target). The white arrow marks the Y-dopant peak

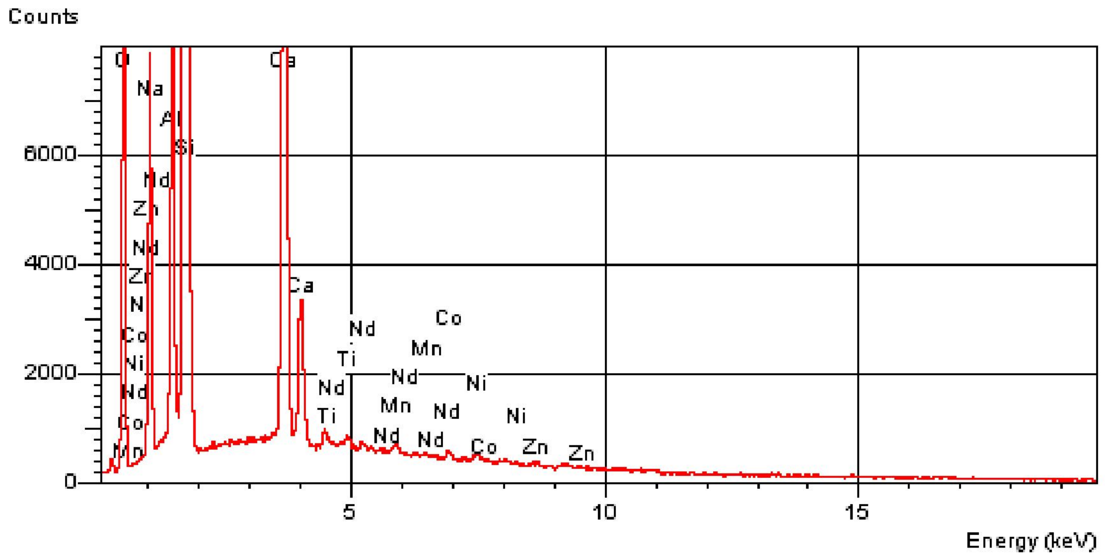

Fig.4a
EDS spectrum of a glass standard (20 kV)

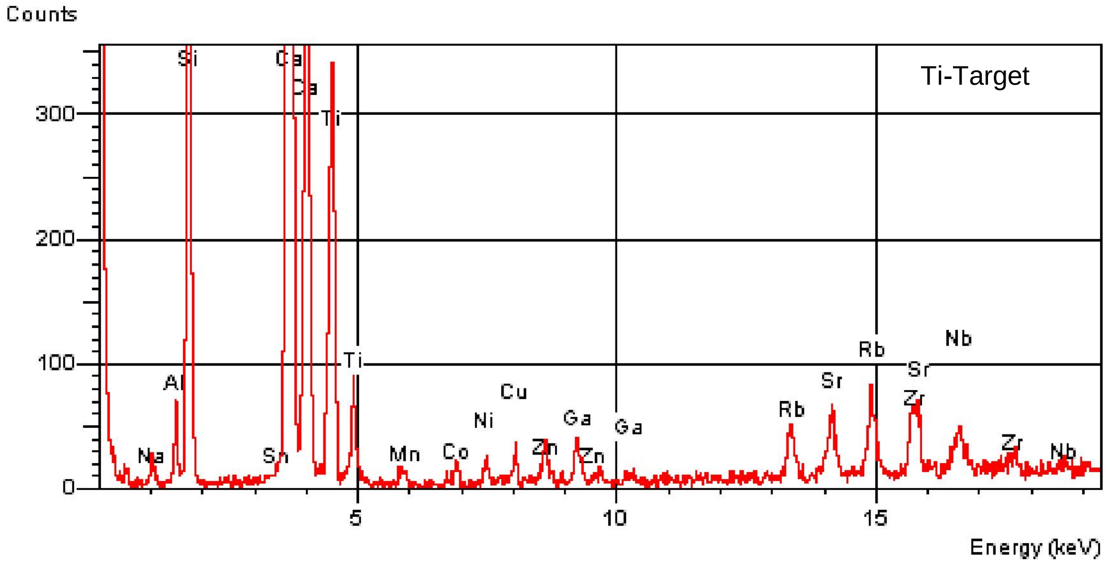

Fig.4b
SEMRAY XRF spectrum of a glass standard as in Fig.3a (Ti-target)

2. Bariumtitanate Ceramics

Bariumtitante Ceramics are often used as a basis material for capacitors or temperature-sensitive resistors. Their electrical properties mainly depend as well on sintering conditions like sintering temperature or sintering atmosphere as on dopant concentrations. Already trace concentrations of rare earth dopants can change significantly the electrical conductivity.

Instrumentation

The SEMRAY-system is designed to enable a routine operation under standard conditions of sample and beam geometry, as well as routine use together with an EDX-detector installed in an SEM. SEMRAY is compatible with all other devices inside the chamber of the SEM.

SEMRAY is permanently flange mounted onto the microscope chamber (compare fig. 3a), and thus is rapidly ready for use. The flange connection is done horizontally, most suitably in a 90°-position with respect to the detector. All settings and adjustments on SEMRAY can be carried out under vacuum. A movable target holder carries the different target foils.

In a stand-by position, the target holder kept completely inside the bellows of the vacuum passage, so as not to disturb normal electron optical work or electron probe EDS-analysis on the sample. If needed, the target holder is driven out of its stand-by position into the optical path of the SEM by horizontal movement of its support shaft. Scales on the rotary knobs for linear shift and three-dimensional xyz-adjustment enable the target position to be set reproducibly.

The rod-shaped target holder is equipped with 6 positions for measuring. These are one open bore to be used for beam adjustment and sample observation (selection of measuring area on sample) and successively 5 inlays of target foil, arranged with increasing atomic number (Al, Ti, Cu, Mo, Ag).

Due to scattering, spectra always include the element peaks of the target material. If the specimen under investigation contains the target material, it is of course obvious to measure the sample with a different target.

Possible Applications

- Identification of certain heavy metal traces as impurities in steel or other alloys/metals
- Detection of material damage due to slight depositions or microreactions on surfaces
- Investigation of trace element characteristics of ceramics, glasses and minerals
- Identification of heavy metals in environmentally relevant samples In general: Detection of heavy elements in a chemically light matrix (i.e. matrix poorly sensitive to excitation)

Application Examples

1. Glass Standard

Glass is a material with a high solubility for almost all elements. It is therefore well suited as a standard for trace element concentrations. Such glass specimens are available as certified NBS standards with chemically analysed trace elements concentrations. SEMRAY XRF investigations conducted on such standard specimens reliably show the accuracy of the method. Fig.4a shows the EDS spectrum of the Glass Standard DLH10b. Clearly, the elemental components of the glass matrix and the Bremsstrahlung share can be recognized. But there are no hints to any other elements contained.

Fig. 4b shows the SEMRAY XRF spectrum of the same specimen. The glass components remain unchanged, but the Bremsstrahlung share has vanished. Instead, a lot of trace elements like Rb, Sr, Nb or Zr occur. Exemplarily, the concentration of Rb is given by 363 ppm and Rb occurs as a significant peak in the spectrum. This shows the high efficiency of the method.

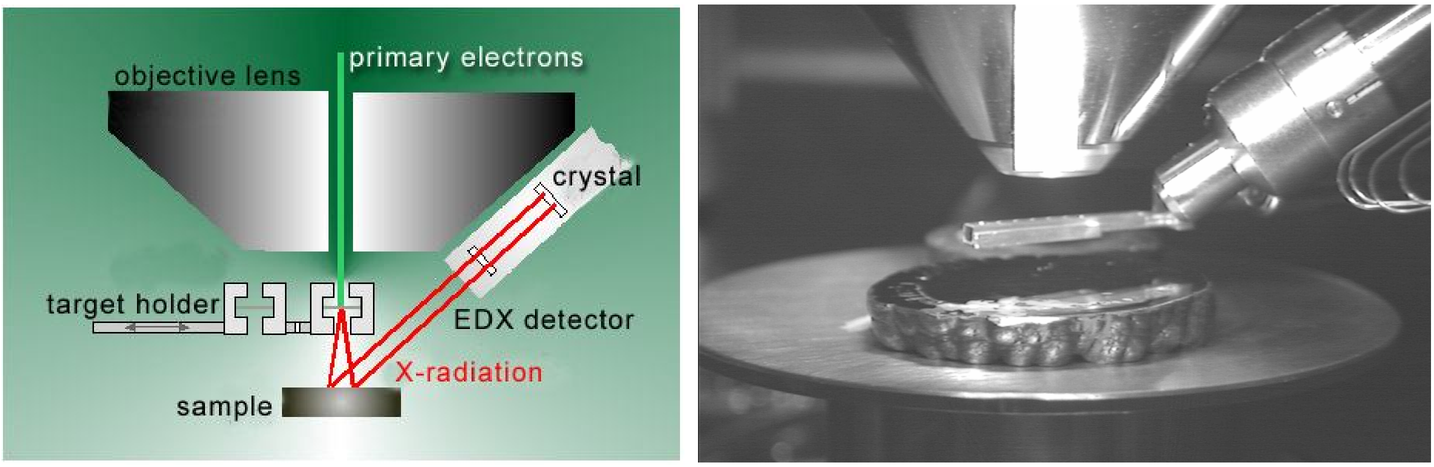

Fig. 2
a (left) : Functional Principle of X-Ray Fluorescence Measurement in the SEM (green : primary electron beam, red : X-Ray radiation). The target holder contains five metal foils in adjacent collimator like bore-holes
b (right) : SEMRAY target holder in measurement position inside the Gemini chamber (right : EDS detector and chamber SE detector)

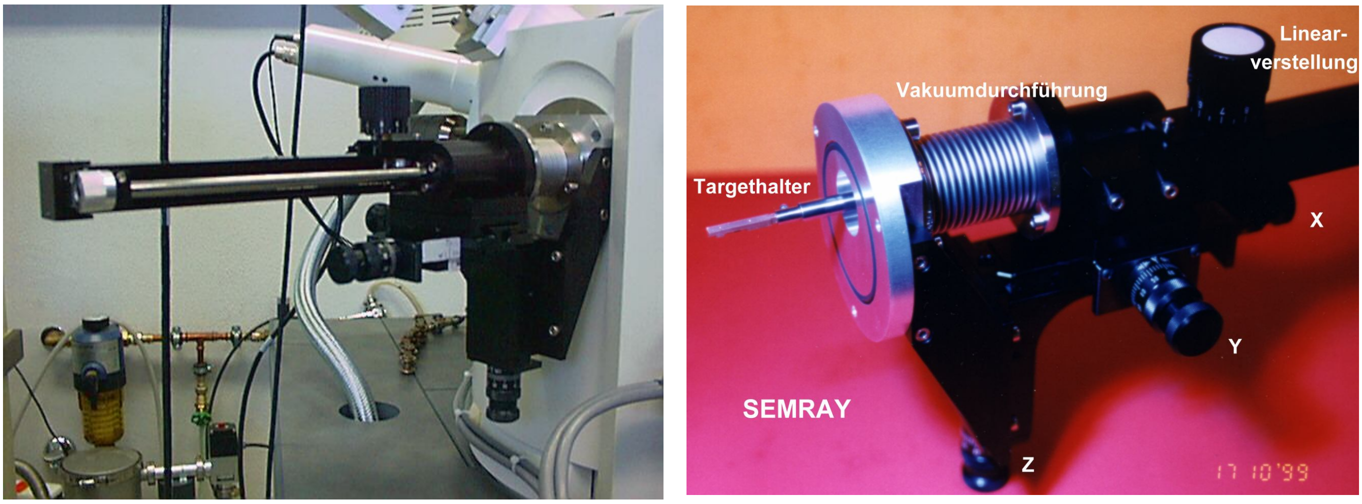

Fig. 3
a (left) : SEMRAY mounted on the Gemini chamber (transition shaft and xyz-adjustment device)
b (right) : front view of the adaptation flange and the vacuum feed through

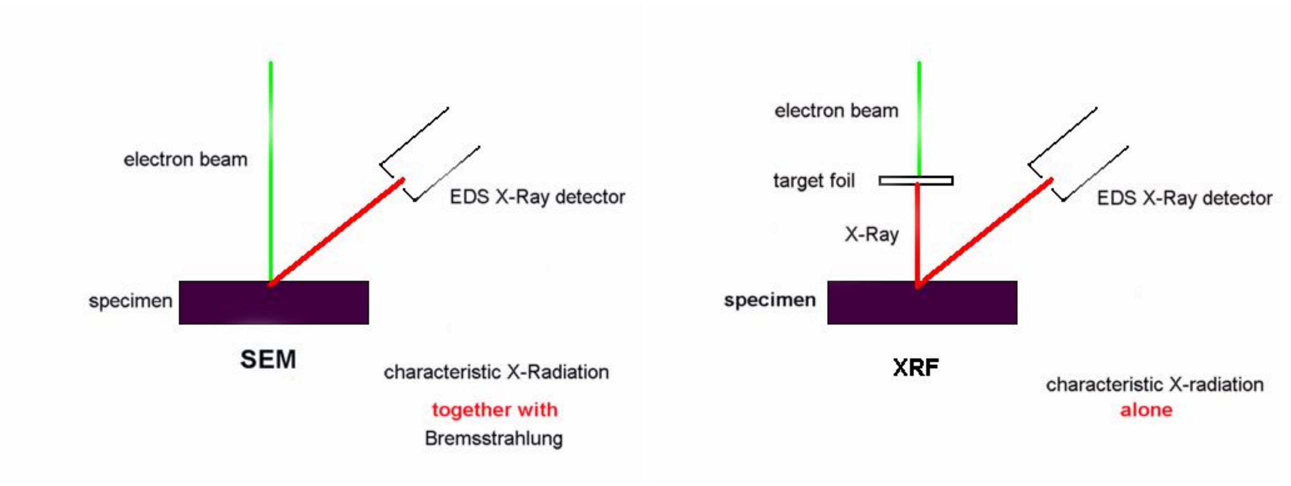

Fig.1 Creation of X-radiation
a (left) : by electron beam excitation the specimen emits a chracteristic X-ray spectrum together with continuous Bremsstrahlung
b (right) : by inserting a metal foil into the electron beam path, X-radiation of the metal foil impinges the specimen and a characteristic (fluorescence) X-ray spectrum is emitted

Because the energy of the X-radiation may not be changed by variing the acceleration voltage of the SEM, instead a variety of foils has to be provided to achieve the desired energy variation as shown in the following table :

Target	**K_α/kV**	**L_α/kV**
Al	**1.48**	
Ti	**4.50**	**0.45**
Cu	**8.04**	**0.93**
Mo	**17.44**	**2.29**
Ag	**22.1**	**2.98**

In the sample, the X-radiation coming from the target causes a fluorescence radiation being free from any detrimental background, and this radiation is recorded in usual manner by the energy dispersive X-ray detector and analyser. Qualitative evaluation of the resulting spectra is carried out by conventional routines. As the spatial resolution is reduced for X-rays, the analysis represents a wider sample area as compared to conventional EDS-analysis with electron excitation. Nevertheless, the information area may be much smaller than compared to stand alone XRF systems and lies in the range of about 50 - 1000 µm. The functional principle is shown in Fig.2.

SEMRAY

Scanning Electron Microscope
X-Ray Fluorescence Measurement Attachment

For the X-Ray Microanalysis down to the ppm range (in addition to EDS-Systems)

Introduction

Users of scanning electron microscopes with EDS-systems know well about the limiting effect of high X-ray background on the desired analytical detectability for low concentrations. Strong background intensity results from deceleration of the exciting electron beam inside the sample (Bremsstrahlung). Varying with element, spectral line under detection, matrix influence and peak overlap, element concentrations may be analysed merely down to the range of 0,7% - 0,1%. Trace elements with concentrations below 1000 ppm escape from reliable detection.

A further limitation concerns the EDS analysis of matrix properties in layered specimens. Layers have certain thicknesses being often higher than the penetration depth of electrons even at high acceleration voltages (~ 2 - 3 µm). In most cases it is not possible to investigate the bulk properties without partly complicated and time-consuming delayering processes.

These disadvantages of EDS-analysis in an SEM can be eliminated by causing excitation of the sample not with electrons but with X-rays. As a result, because of the missing background the detection limit is increased to some ten ppm and - because of the higher penetration depth of X-rays compared to electrons - matrix or bulk effects can be investigated without delayering the specimen. This could be done by an XRF-analysis inside the scanning electron microscope. However, compared to EDS stand-alone XRF systems show only poor spatial resolutions in the range of mm.

Best results may be obtained by a combination of the two analysing methods in the SEM. The SEMRAY XRF attachment accomplishs this demand and considers the following requirements :

- simple Adaption
- no limitation of other Measurement Possibilities
- easy to operate, easy to change, retractable, adjustment under vacuum
- Improvement of the spatial resolution compared to XRF down to some ten µm

Function Principle

Between electron source and sample, a metal foil (target) is positioned as `X-ray generator´ within the beam path of the SEM (see Fig.1a,b). When the electron beam strikes the metal foil, upon deceleration in the target it causes an excitation of the metal atoms and thus emission of the full X-ray spectrum of the target material. This (primary) X-radiation is filtered by passing through the target foil, is collimated by the specific geometry of the target holder and finally is used to irradiate the sample. No external X-ray tube is needed. Concerning the target foil, logically it is understood that it must be thick enough to absorb all electrons with energy up to the acceleration voltage used, and it must be thin enough to ensure a sufficiently high transmission of X-rays.

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X-Ray Fluorescence Measurement System for Scanning Electron Microscopes

SEMRAY

System Description and Application Examples