

Wavelength-Dispersive Fluorescence (WD μ XRF) Micro X-Ray Analysis with the microprobe

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Abstract. An Electron Probe Microanalyser (EPMA) determines the element distribution by detection of the electron beam excited characteristic X-rays using wavelength-dispersive spectrometers (WDS). This study evaluates the benefits of implementing a micro-focus X-ray source into the EPMA as an alternative excitation of X-Ray fluorescence (WD μ XRF). Since XRF does not generate a Bremsstrahlung background, a higher detection limit is anticipated for elements with atomic numbers greater than 20 [1]. However, differing excitation probabilities and space constraints may result in lower overall signal intensity and a higher signal-to-noise ratio (SNR). This paper reports the mechanical integration of a IFG-IMOX X-ray source into a JEOL JXA-8530F electron microprobe. The signal-to-noise ratio (SNR) shows that WD μ XRF performs comparably to conventional WD-EPMA under standard beam conditions of 20 kV and 500 nA. However, when using a fresh electron source with higher beam currents (1.9 μ A) or increased accelerating voltages (30 kV), WD-EPMA exhibits superior SNR at identical measuring times, resulting in improved detection limits. We identify key parameters to enhance WD μ XRF performance. Additional advantages of WD μ XRF are also discussed, including the suitability for insulating materials, layered structures, rough surfaces, and beam-sensitive specimens. These factors make WD μ XRF an attractive alternative, even in cases where the signal-to-noise ratio is lower compared to WD-EPMA.

1 Introduction

Electron beam-excited, energy-selective detection of characteristic X-rays (SEM/EDS) enables both qualitative and quantitative element analysis in a scanning electron microscope (SEM) with high spatial resolution. The limited detection sensitivity of the SEM-EDS analysis can be improved with two extensions of the SEM. Firstly, the characteristic X-rays of the EDS analysis can be excited using X-rays. This X-ray fluorescence analysis (XRF) is a widely used analysis method in the field of materials science, mineralogy and semiconductor technology, among others [2, 3]. The spatial resolution can be increased by focussing the exciting X-ray beam with a polycapillary lens (μ XRF), so that integration of such an X-ray source into an SEM enables simple correlative measurements of SEM surface images as well as SEM-EDS and μ XRF-EDS element analysis. The μ -XRF has the advantage

of a higher detection sensitivity, since no bremsstrahlung is excited and thus the background for elements $Z > 20$ is significantly lower.

Fig. 1 illustrates an example of a comparison between an X-ray excited EDS spectrum (red) and an electron beam excited EDS spectrum (blue) of an aluminium sample holder. Note that the heavy elements lead and bismuth could be detected with X-ray excitation, but not with electron excitation [4]. Furthermore, it can be seen that there is no bremsstrahlung in the case of X-ray excitation, so that the detection limit is significantly reduced.

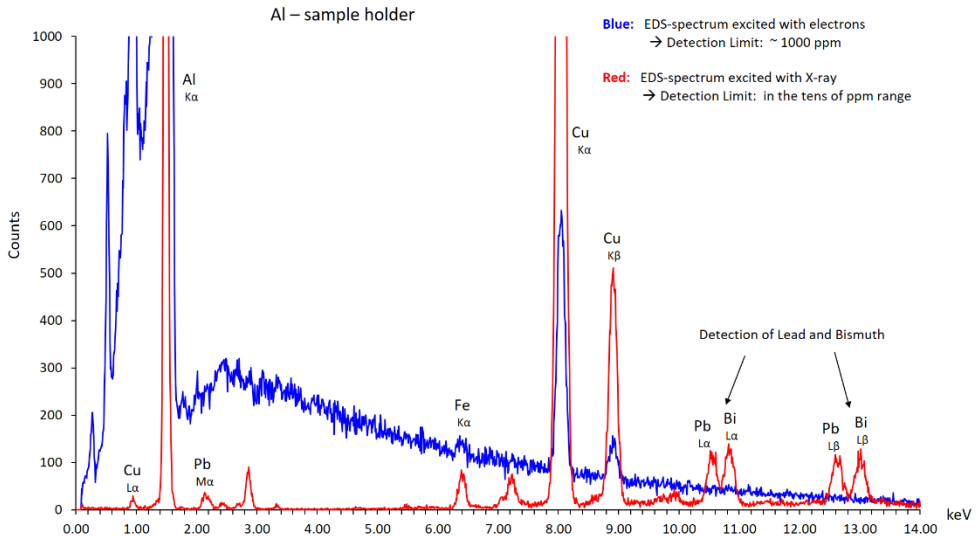


Fig. 1. X-ray excited EDS spectrum (red, without bremsstrahlung) and electron beam excited EDS spectrum (blue, with bremsstrahlung) of an aluminium sample holder

Another advantage of X-ray fluorescence analysis may be that larger volumes can be analysed due to the greater range of the X-rays, which means that on one hand, averaged values of element distribution can be obtained, while on the other hand, information hidden below the surface (e.g. multilayer systems) can be analysed (although the matrix correction may not be quite as accurate). Moreover, it is possible to investigate non conductive samples as there are no charging effects due to electrons. In addition, samples with very strong surface topography such as fracture surfaces can be analysed. The X-ray beam also prevents carbon contamination and beam damage of the sample surface. The exciting X-rays cannot be focused as well as electron beams, but this is not a disadvantage in the above mentioned cases.

The second well-known method for improving the detection limit of SEM/EDS is to use wavelength-dispersive spectrometers (SEM-WDS) instead of energy-dispersive spectrometers (EDS). These crystal spectrometers have a significantly better spectral resolution, which consequently improves the detection sensitivity. In order to fully exploit this advantage, this detection method is used together with specially stabilised SEMs, which are referred to as electron probe microanalysers (EPMA) or microprobe for short. Unfortunately, however, even in the microprobe, the coexcited bremsstrahlung underlays the spectra. Therefore, the aim of this work is to experimentally test whether and under which circumstances the integration of a μ -focus X-ray source into a microprobe can combine the advantages of both worlds to further increase the detection sensitivity.

2 Experimental and results

2.1 Setup and adjustment of the X-ray source

For the experimental setup we attached a standard X-ray source (iMOXS by IFG) with rhodium target and focusing polycapillary optics (spot size: $\sim 100 \mu\text{m}$) to our JEOL JXA 8530-F microprobe at the port that is actually intended for the CL spectrometer (Fig. 2). The X-ray source must be specially adapted to this port, which in our case required a customised polycapillary lens with a focal length of around 50 mm and a special adapter.

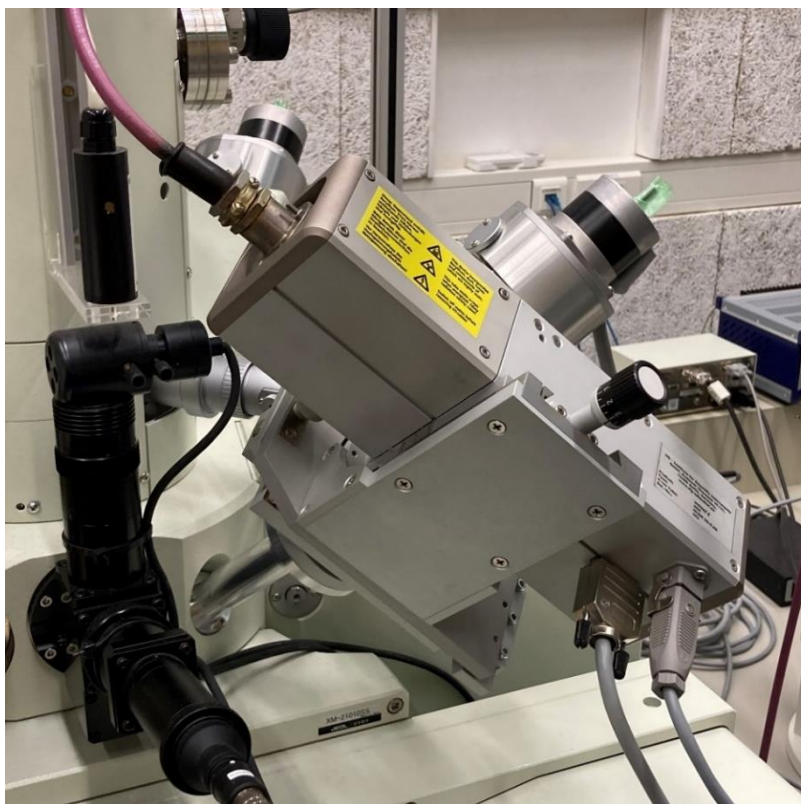


Fig. 2. X-ray source iMOXS attached at CL-port of the microprobe

The X-ray source must be adjusted in the X and Y directions so that the X-ray beam and the electron beam hit the same sample surface position. The adjustment of the microprobe ensures that this is also the source point of the Rowland circle of the spectrometers. A sample with 4 concentric rings of different elements (Zn, Cu, Ni, Fe) is used for the adjustment of the X-ray source (Fig. 3). The adjustment is optimized when the maximum intensity of the Fe-K line in the EDS spectrum (Fig. 4) is obtained from the center of the sample, which is an iron wire with a diameter of $65 \mu\text{m}$. First, the x/y positions of the source and then the distance to the sample surface are optimised. Special care must be taken to ensure that the polycapillary lens does not touch the pole piece of the microprobe in order to avoid ground loops and vibration coupling. Fig. 5 shows the polycapillary lens of the iMOXS before and after adjustment.

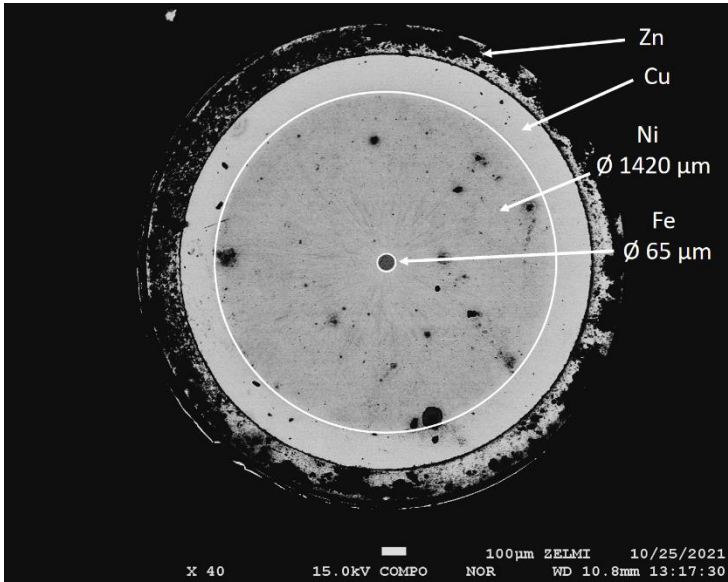


Fig. 3. Adjustment sample with 4 concentric rings of the elements Zn, Cu, Ni and Fe

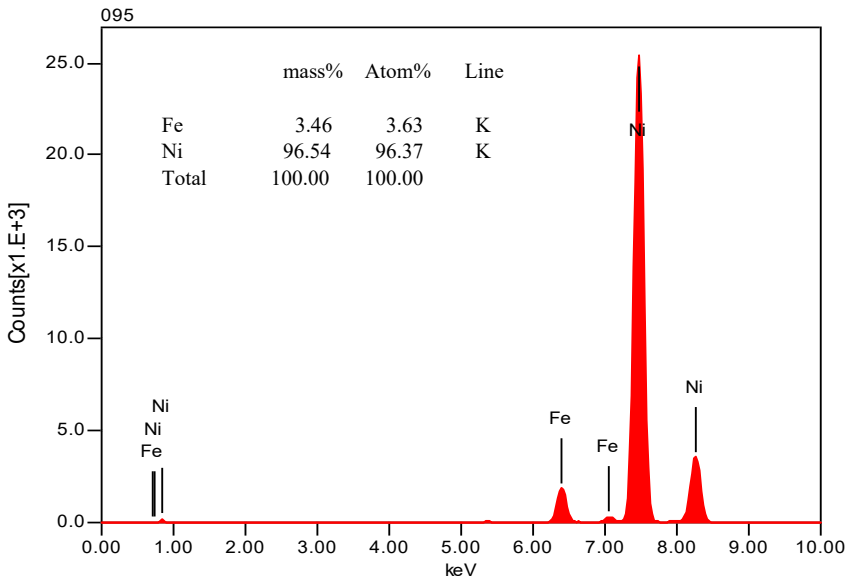


Fig. 4. Intensity of the Fe K α -line after X-ray source adjustment

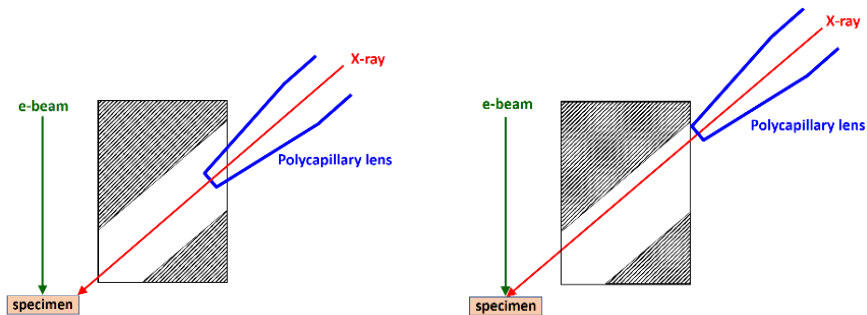


Fig. 5. Polycapillary lens of the iMOXS before (left) and after adjustment (right)

2.2 Test specimen

The detailed measurements to compare the detection sensitivities of electron beam and X-ray excited EDS and WDS spectra were carried out using a multicomponent glass from the former Brei \ddot{u} ndler company (Fig. 6). It has a polished surface and is coated with an approximately 10 nm thick carbon coating. Unfortunately, no calibrated element composition is available, but this does not affect our objective of a relative comparison of different methods. Over the course of our investigations, the elements V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Nb, Mo, Sn, Sb, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Hf, Ta, W, Pb, Th, U were found, many of which only have a concentration of just a few tens of ppm.

Fig. 7 shows a comparison of the X-ray excited WDS spectrum (red, LIF crystal) and X-ray excited EDS spectrum (green) of multicomponent glass for the energy range 7.1 to 10.0 keV. Due to the better spectral resolution of the WDS spectrometer, the detection of a few tens of ppm Sm, Dy, Yb, Ho, Er and Hf is possible.

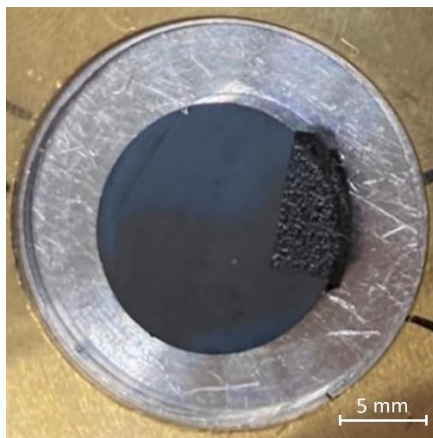


Fig. 6. Brei \ddot{u} ndler multicomponent glass (top view)

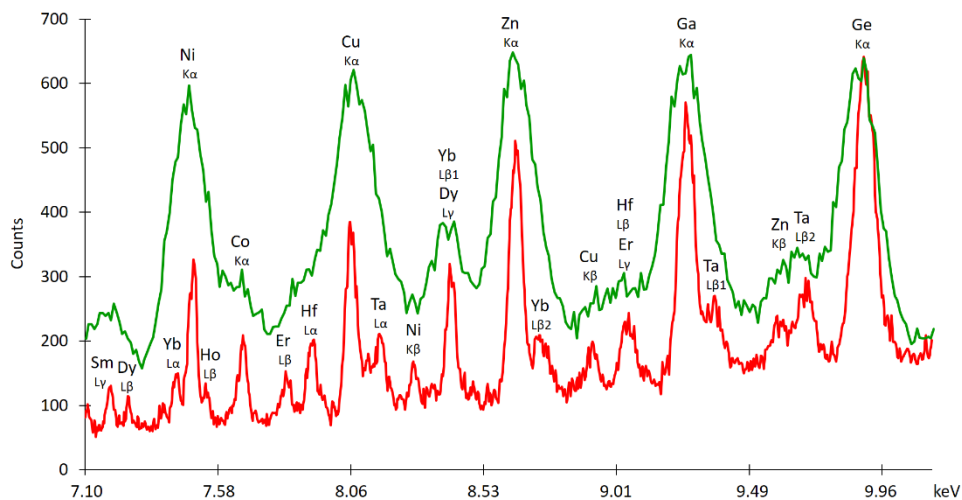


Fig. 7. X-ray excited WDS spectrum (red, lower) and X-ray excited EDS spectrum (green, upper) of multicomponent glass for the energy range 7.1 to 10.0 keV

2.3 Measurements and results

As a user of a typical microprobe whose electron source is optimised for high beam currents in the μA range, it is somehow easy to forget how low the excitation probability of the characteristic X-rays and how low the sensitivity of double-focused crystal spectrometers are. We are painfully reminded of this when the excitation is carried out by a laboratory X-ray source with a polycapillary lens, whose X-ray radiation at the Rh target itself is only excited with a maximum electron current of 1 mA, which leads to a very low excitation X-ray intensity. After fluorescence excitation and wavelength selection in the spectrometer, a signal often remains that corresponds to less than one hundredth of the usual signal. This sounds dramatic, but it has not stopped us from continuing our investigations, as our aim is to improve trace element analysis. Although it might prove inconvenient to have to analyse one point for up to an hour, rather than the typical 30s, having access to trace element analysis is highly desired.

We present measurements of WDS spectrometer scans with nearly 4000 steps at a measurement time of 100 s per step. The total measurement time of 110 hours per spectrum is an impressive test of the device's stability, but it should not be forgotten that the complete spectrum is never necessary for the subsequent detection of a trace element.

In order to compare the advantages and disadvantages of electron beam and X-ray excited analyses, we carried out three measurements with different parameters:

1. Excitation with $\mu\text{-X-ray}$ source with tube settings 37 kV, anode current 800 μA
2. Excitation with electron beam, 20 kV, 500 nA, probe diameter 300 μm
3. Excitation with electron beam, 30 kV, 1.9 μA , probe diameter 300 μm

In the second case scenario, the settings are typical for trace elements with a beam current that FEG electron source still provide after several years of operation. As for the third case, this represents a newly installed FEG source with maximum beam current. Of course, these

high electron beam currents can only be used with suitable samples. When analysing glass or if alkali drift is a concern, significantly lower beam currents may need to be used for electron beam excitation. In this case, X-ray excitation has a clear advantage.

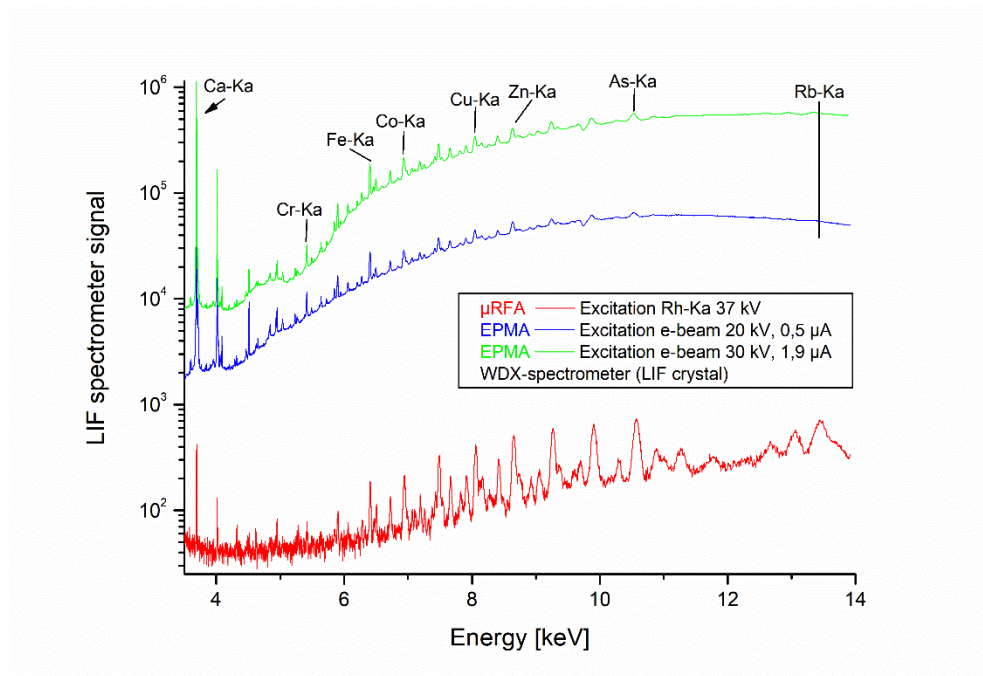


Fig. 8. Complete LIF-spectrometer scans on “Breitländer” multicomponent glass with different excitation sources and settings

The μ XRF-spectrum shows the absence of Bremsstrahlung generated in the specimen but still some “spectrometer” background due to Compton- and Rayleigh-scattering of the Bremsstrahlung generated in the X-Ray tube. Also, the decrease in spectral resolution at low wavelengths is present. Both EPMA spectra, on the other hand, show the excited and detected bremsstrahlung including a deficiency peak due to double diffraction. In addition both EPMA-spectra have higher net peaks at low energies and smaller peaks at high energies. All the above-mentioned and other characteristics of the spectra can be explained by the overvoltage ratio of the excitation and the excitation probabilities of the X-ray emission.

Coming back to the original aim of the investigation, the evaluation of the detection sensitivity, the spectra seem to show that the peaks above approx. 6 keV are more distinct in the case of X-ray excitation (red spectrum). For a better assessment, Fig. 9 shows a section of the spectrum in which the background has been subtracted and all spectra have been normalised to the intensity of Ca-Ka.

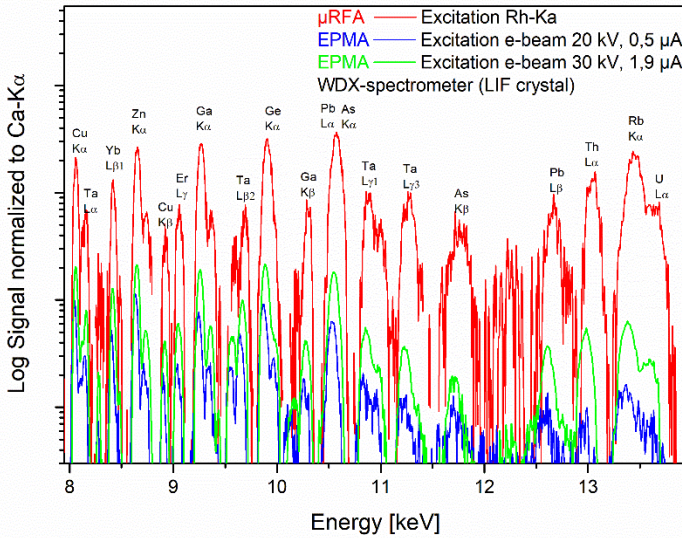


Fig. 9. Logarithmic plot of X-ray excited (red) and electron beam excited (blue and green) WDS spectra of multicomponent glass measured with the LIF crystal (background subtracted, normalized to Ca K α at 3.69 keV)

Due to the normalization, the XRF-spectrum has higher signal and less noise compared to the 20kV/0.5 μ A e-beam excited spectrum (blue) at identical acquisition times. These e-beam settings are close to real-world EPMA-analysis even with a slightly aged FEG-source. For the maximum 30kV/1.9 μ A e-beam setting (green) the signal-to-noise ratio is higher compared to the XRF-spectrum. For a detailed analysis of the signal strength and noise, two parameters are determined from the spectrum in Fig. 8, with averaging performed in intervals approximately 100 eV wide around the peaks:

1. **Peak-to-Background ratio:** the spectra are smoothed to compensate for noise fluctuations, then the net count intensity is divided by the background level, no matter if background is caused by Bremsstrahlung or by the spectrometer itself
2. **Relative Background Noise Amplitude:** the maximum noise amplitude is divided by the smoothed, averaged background level

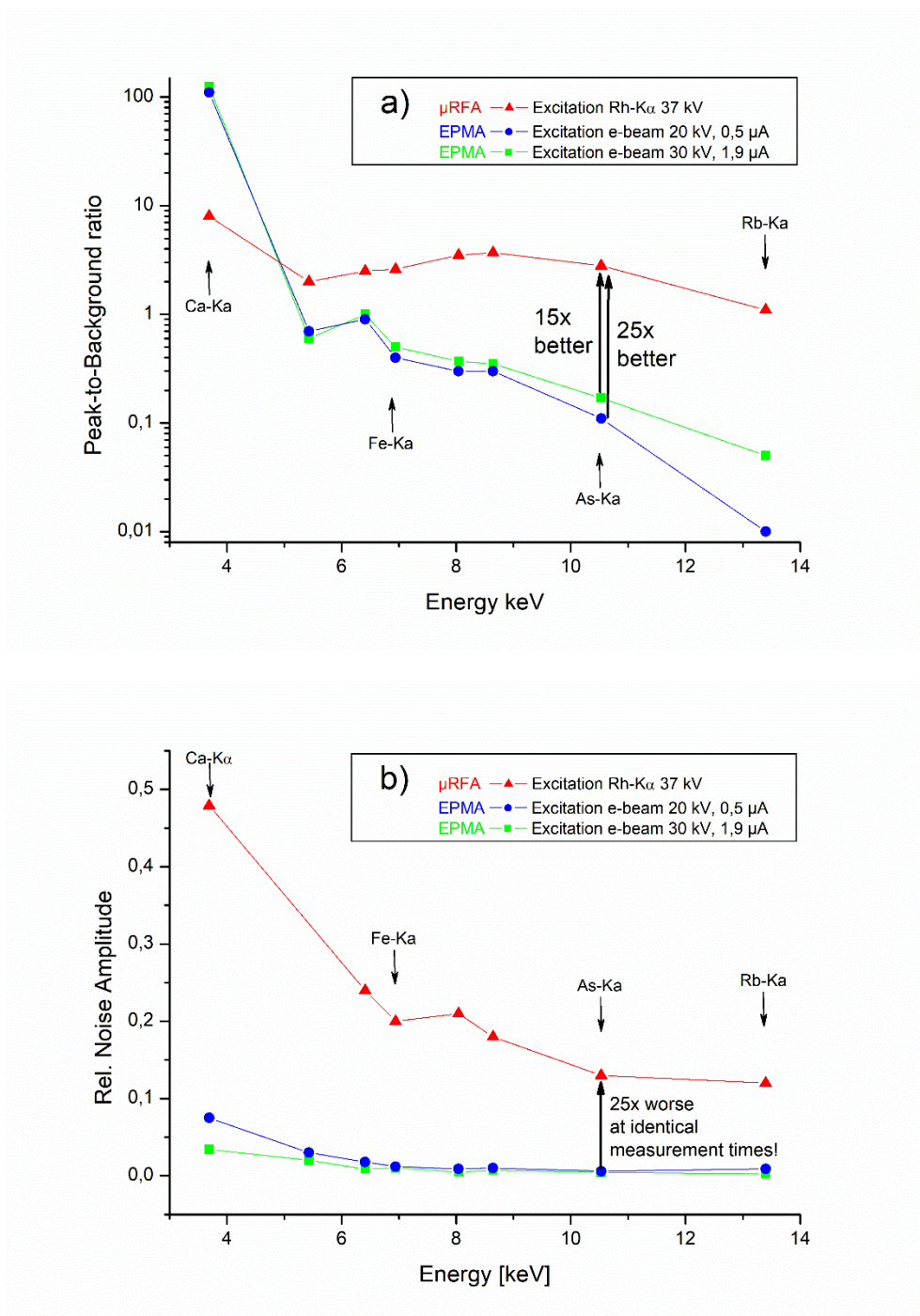


Fig. 10. a) Calculated **Peak-to-Background ratios** for element lines indicated in Fig. 8;
b) Calculated **relative background noise amplitudes** for the same element lines

From Fig. 10 a) we can conclude that in the x-ray excited spectrum, lines above approx. 4 keV are more clearly visible above the background, since no bremsstrahlung occurs. In the case of As-K α the gain is a factor of 15 and 25 for the 30 kV and 20 kV excited electron beam spectra, respectively. This seems to prove the superiority of μ XRF in the microprobe. Unfortunately, however, the evaluation in Fig. 10 b) shows that the noise level is 25 times higher at the same time. This means that the detection limit is absolutely identical for both electron beam excitation and X-ray excitation, in the case of typical excitation parameter of 20 kV and 500 nA of an aged FEG source. In the case of a new FEG source with higher beam current, electron beam excitation is more efficient in terms of detection limit since the noise is smaller. Having said this, it is clear how the X-ray excitation needs to be improved to even exceed the detection limit of the best possible electron beam excitation:

1. A modern laboratory X-ray source for SEM has a 25% higher anode current, thus a 25% higher signal-to-noise ratio.
2. Modern polycapillary lenses provide much smaller focus spots that are claimed to be down to 5 μ m. In this case the vignetting of the crystal spectrometers is much less. Fig. 11 shows the spectrometer detector signal variation of a 2 mm by 2 mm beam scan on a homogenous sample. Even a 30 μ m spot instead of the 100 μ m spot of the used X-ray source would increase the detector signal by a factor of 25 %.
3. The measurement time should be increased by a factor of at least 25 compared to e-beam excitation.
4. The detectable energy range should be extended to higher energies, since Fig. 10 clearly shows that the peak to background ratio increases and the noise level decreases with higher peak energy. Unfortunately, the detectable energy of WDS is limited so far to 14 keV. Therefore, crystals with lower atom distances or lattice parameters are required to get the full benefit out of WD μ XRF in a microprobe.

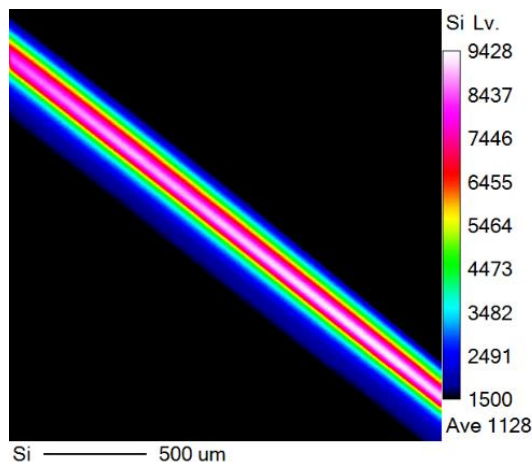


Fig. 11. Vignetting of spectrometer with Ar-counter on a JEOL Microprobe JXA-8530F for a 2 mm x 2 mm beam scan on a Si-Wafer

We have thus clarified the possible concept with which X-ray excitation on a microprobe can increase the detection limit without competition. But even without these steps, X-ray excitation at the microprobe has decisive advantages.

Beam Damage:

The X-rays do not heat up the specimen as strong as high electron beam currents do. The glass surface in Fig. 12 right shows strong modifications after the 30 kV / 1.9 μ A e- beam excitation over 110 hours even at a strong defocus of 300 μ m beam diameter while the structure of the surface is preserved even after 110 hours of X-ray excitation, Fig. 12 left.

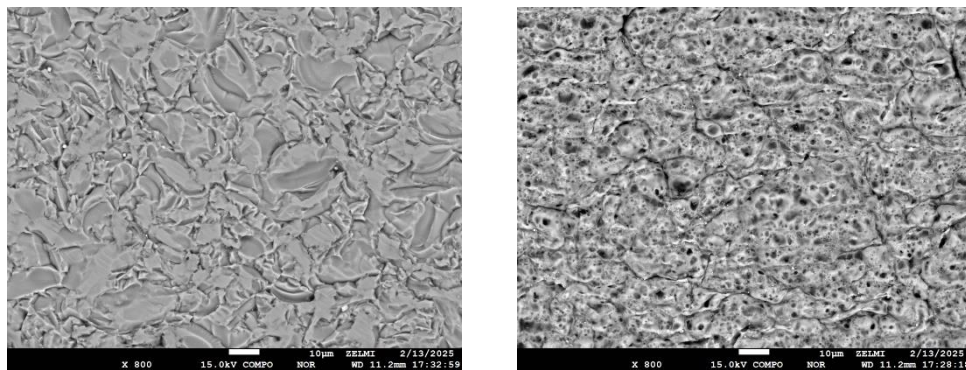


Fig. 12. Left: Glass surface after X-ray excited WDS measurement → No beam damage !
Right: Glass surface after E-beam excited WDS measurement → Strong beam damage !

Non conducting Specimens:

Obviously, the x-ray beam does not cause charging of insulating specimens. Therefore, the excitation energy is not changed and quantification routines are more reliable in comparison to e-beam excitation of isolators. Moreover, the beam neither oscillates nor moves during analysis.

Analysis of multilayer specimen:

The electron beam excited WDS spectrometry always analyses the top 1- 2 μ m of the surface at the most. The penetration depth of X-rays might be up to several tens of μ m. Therefore, hidden layers can be discovered and their (quantitative) element distribution can be determined with appropriate software.

3 Conclusions

A focused X-ray source is a valuable enhancement to extend an EPMA system into a wavelength-dispersive micro-XRF (WD μ XRF) system. Integrating a commercial X-ray source via the CL port and aligning it mechanically is relatively straightforward. A WD μ XRF setup offers numerous benefits for a wide range of samples, including insulators, beam-sensitive materials, specimens with significant surface topography, hidden layers, or cases where bulk averaging of heterogeneous materials is desired.

In our configuration, the detection limits of WD μ XRF are comparable to those of EPMA under standard excitation conditions (20 kV, 500 nA). However, to match the signal-to-noise ratio (SNR) achieved with EPMA at its maximum settings (30 kV, 1.9 μ A), WD μ XRF would require measurement times approximately 25 times longer. Therefore, an X-ray source with higher flux in combination with improved focusing capillary optics would be of great benefit for general applications. When analysing radiation-sensitive samples that cannot tolerate the high electron currents of EPMA, like glasses or if alkali drift is a concern, the X-ray source used here already offers better signal-to-noise ratios and better detection limits.

The key strength of WD-XRF lies in its lower spectral background, due to the absence of Bremsstrahlung, which allows for cleaner spectra. This advantage could be exploited to additional elements—provided that WD spectrometers with enhanced spectral resolution above 8 keV and an extended energy range beyond 14 keV are available. This would necessitate the use of crystals with smaller atomic spacing or higher lattice planes.

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