



MICRO-XRF ON SEM

Comparison of element detection in a certified aluminum alloy with EDS and micro-XRF on SEM

Application Note # MXRF-SEM-02

Introduction

Aluminum alloys are often used in the aircraft and automotive industry as they combine the light weight of the aluminum with the mechanical properties of the specific alloy. The elemental composition is crucial for the properties of the alloys, since even small amounts of additives influence the mechanical and thermal properties of the material.

The investigation of aluminum alloys using micro-X-ray fluorescence spectroscopy (micro-XRF) in the scanning electron microscope (SEM) is especially promising due to the higher sensitivity of element detection ($Z > 20$).

The example demonstrated here shows the improvement of trace element detection in a certified aluminum alloy (Alcoa Deltalloy[®] 4032, Figure 1) with micro-XRF on SEM.



Figure 1

Photograph of the analyzed specimen Alcoa Deltalloy[®] 4032

Methods

XTrace is a focused X-ray photon source, which allows micro-X-ray fluorescence spectrometry (micro-XRF) performing in a scanning electron microscope (SEM). This combination extends the analytical capabilities of the SEM to trace element detection at ppm level. In comparison to SEM-EDS, the X-ray source on a SEM significantly increases the detectability for elements with an atomic number higher than 20.

In comparison to electron excitation, the photon excitation causes a lower spectral background as no bremsstrahlung is generated in the sample. This results in a better peak to background ratio. In combination with the possibility to effectively excite the high energy lines over 15 keV, the problems resulting from overlap between neighboring peaks are reduced.

Micro-XRF can achieve a detection limit down to 10 ppm ($\mu\text{g/g}$). The limit depends on the element and the sample matrix (Figure 2). For comparison, EDS can only detect elements down to 1000 ppm (0.1 mass%).

In general, the sensitivity of detection for elements heavier than calcium is higher using

micro-XRF than the electron beam (Figure 2). Furthermore the X-ray excitation provides compositional information not only from the sample surface as in case of the SEM but also from several microns depth.

Measurement conditions

For this case study, a SEM was equipped with a Bruker QUANTAX system consisting of a 30 mm² active area silicon drift detector (SDD) XFlash[®] 6I30 with an energy resolution of 123 eV for Mn K α and the XTrace source with a Rh-anode X-ray tube. The SEM was used for electron excitation, whereas the XTrace was used for photon excitation. The XFlash[®] SDD detects X-rays generated by both sources, electron and photon excitation.

For analysis, 10 point spectra were acquired with each technique on the same sample area using separate and consecutive electron and photon excitation. A standardless fundamental parameter algorithm was used for XRF quantification. The EDS quantification results were obtained using a peak-to-background quantification method (P/B-ZAF). Table 1 summarizes the used measurement conditions and the elements detected by both excitation methods.

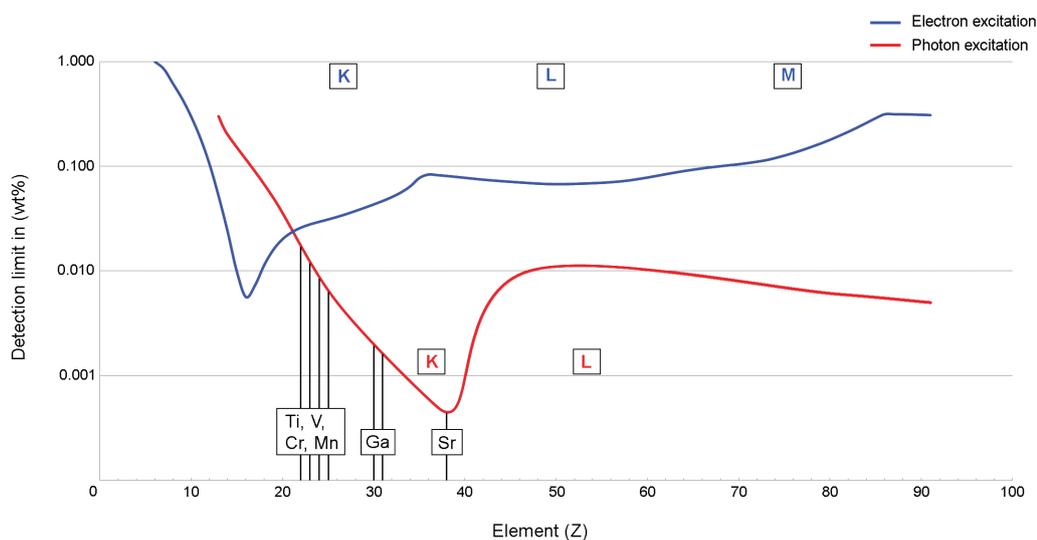


Figure 2

Estimated detection limits for photon excitation (red) and electron excitation (blue). They depend on the element and the matrix composition. In general, micro-XRF improves the detectability of elements above atomic number 20 (calcium) - compared to SEM-EDS. Only micro-XRF detects the elements shown in black, their concentration is below or close to the limit of detection for electron excitation.

| Excitation | Voltage, current | Input count rate (ICR) | Acquisition time | Detected elements |
|------------------|--------------------|------------------------|------------------|--|
| Electrons (SEM) | 20 kV | 10.7 kcps | 200 s | Mg, Al, Si, Cr, Fe, Ni, Cu, Zn |
| Photons (XTrace) | 50 kV, 600 μ A | 9.5 kcps | 200 s | Mg, Al, Si, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Sr |

Results

The elements Mg, Al, Si, Cr, Fe, Ni, Cu, and Zn were identified with EDS and micro-XRF (Table 1, Figure 3) in the certified aluminum alloy. The sample also contains different elements in traces. The elements Ti, V, Mn, Ga, and Sr were exclusively detected with micro-XRF. Moreover, the lower detection limit of micro-XRF (Figure 2) allows detecting Cr, Fe, Ni, Cu and Zn with a much better signal to noise ratio.

The standardless quantification results for EDS and XRF are compiled in Table 2. With EDS only the elements Mg, Al, Si, Fe, Ni, Cu, and Zn can be quantified. Zn was quantified only in four out of 10 analysis runs. In the other six analysis runs the element was below the detection limit for EDS.

The micro-XRF spectrum was quantified using a standardless fundamental parameter method. The quantification results illustrate

the element sensitivity of XTrace. Although the concentration of the elements Ti, V, Cr, Mn, Ga, and Sr is below the EDS detection limit of 0.1 mass%, they were detectable and were quantified with micro-XRF.

Chromium could be seen, but not quantified with EDS, because its concentration is below the EDS limit of detection. In contrast, quantification of Cr with micro-XRF is possible due to the better limit of detection.

Furthermore, Table 2 shows the quantification results of EDS and micro-XRF in comparison to the certified values of the investigated aluminum alloy. It can be clearly seen that for most elements the EDS and XRF quantification results are very close to the certificate values.

The slightly larger difference for the Ti concentration between the micro-XRF result and the certified value is caused by an overlap with a diffraction peak.

Table 1

Measurement conditions and detected elements in a certified aluminum alloy. Elements in red were only detected with micro-XRF.

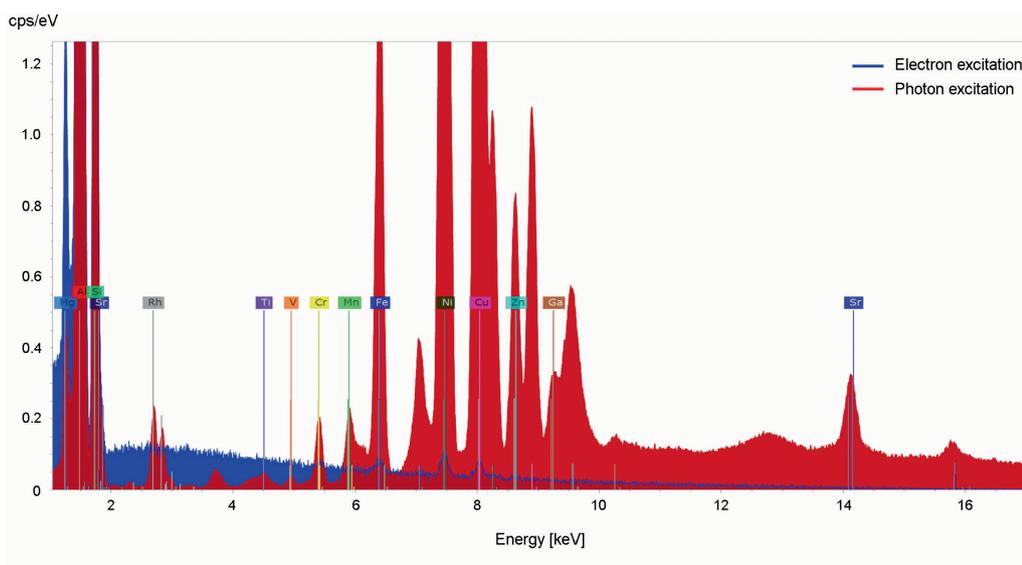


Figure 3

Comparison of EDS (blue) and Micro-XRF (red) spectrum. The element peaks of Ti, V, Mn, Ga and Sr are only present in the micro-XRF spectrum. The Rh-lines derived from the scattered XRF-tube spectrum. Unlabeled peaks are diffraction peaks.

| | Mg | Al | Si | Ti | V | Cr | Mn | Fe | Ni | Cu | Zn | Ga | Sr |
|------------------------------------|------|-------|-------|-------|--------|-------|-------|------|------|------|-------|------|-------|
| EDS mean concentration value | 1.20 | 85.09 | 11.43 | n.d. | n.d. | b.d. | n.d. | 0.36 | 0.91 | 0.91 | 0.10 | n.d. | n.d. |
| Micro-XRF mean concentration value | 0.85 | 83.87 | 12.83 | 0.03 | 0.01 | 0.06 | 0.03 | 0.36 | 0.93 | 0.93 | 0.10 | 0.01 | 0.03 |
| Certificied values | 1.1 | 84.52 | 12.00 | 0.011 | 0.0099 | 0.051 | 0.033 | 0.31 | 0.89 | 0.89 | 0.098 | 0.02 | 0.026 |

Conclusion

Due to the high element sensitivity of micro-XRF five more elements (Ti, V, Mn, Ga, and Sr) were exclusively detected in a certified aluminum alloy by using micro-XRF.

The high sensitivity of micro-XRF for element detection is based on a lower background, a lack of bremsstrahlung and a higher peak to background ratio compared to electron excitation. Therefore, micro-XRF allows a better characterization of the sample.

The standardless micro-XRF and EDS quantification results are close to the certified values.

XTrace is a perfect complementary analytical tool for a SEM to improve the detectability of trace elements.

Table 2

Comparison of the EDS and micro-XRF quantification results with the certified values, element concentration in mass% normalized (b.d. = below limit of detection, n.d. = not detectable)

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