

A vertical decorative image on the left side of the page, showing a bright light source at the bottom center with numerous thin, colorful rays (purple, blue, green, yellow) radiating upwards and outwards against a dark background.

Mitigating Matrix Effects with Advanced Spectra-Handling Functionality When Using XRF for High-Accuracy Elemental Analysis

Introduction

One of the great advantages of X-ray fluorescence (XRF) analysis is its ability to measure samples directly, without time-consuming and destructive sample digestion. Realizing these benefits, however, requires the elimination of potential analysis errors that can result when some atoms in the sample matrix influence the fluorescence of other atoms, thus affecting the intensities measured by the spectrometer. Such effects — which include absorption and enhancement — when taken collectively, are referred to generally as matrix effects. Today, matrix effects are well characterized. Soft-

ware applications such as SPECTRO's TURBOQUANT system can help analyze complex and completely unknown samples in minutes with very high accuracy.

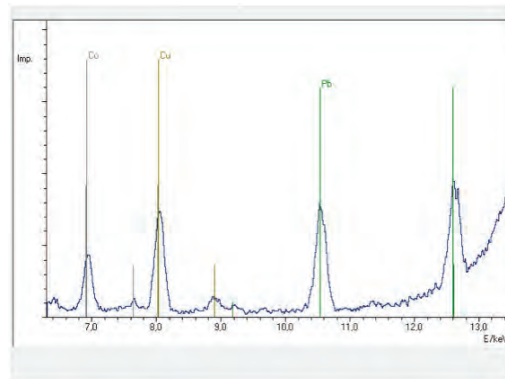
However, creating the right basis for consistently high-accuracy results requires additional spectra-handling functionality to determine the correct net intensities of the measured spectra. This paper explains why this additional functionality is a critical aspect of overcoming matrix effects and ensuring those consistently high-accuracy results.

Effects and their countermeasures

For a sample containing only a few measurable elements at fairly low concentrations, it's quite easy to determine accurate net intensities, as one can imagine from the following spectrum (Figure 1)

Fitting a background, for example, would easily be possible by selecting fit regions on both sides of each fluorescence line and then interpolating the background underneath the fluorescence signal.

Figure 1: Spectrum of a sample containing only a few detectable elements at reasonable concentration levels in linear scale



However, if the sample contains more elements at varying concentration levels, the spectrum may look completely different. Calculating the results would require careful determination of the correct net intensities (Figure 2).

In this case, fitting the right background is no longer easy. Other effects must be considered even before subtracting the background, as illustrated by the following examples (Figure 3).

Figure 2: A more complex spectrum from a sample containing more elements at various concentration levels in linear scale

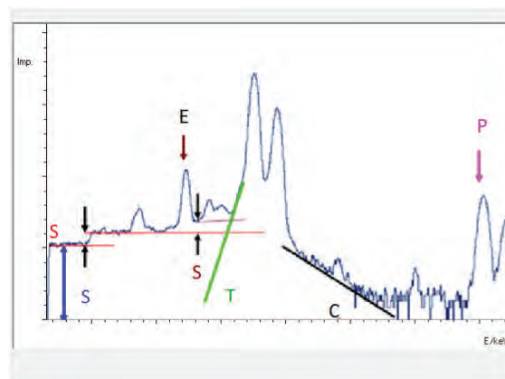
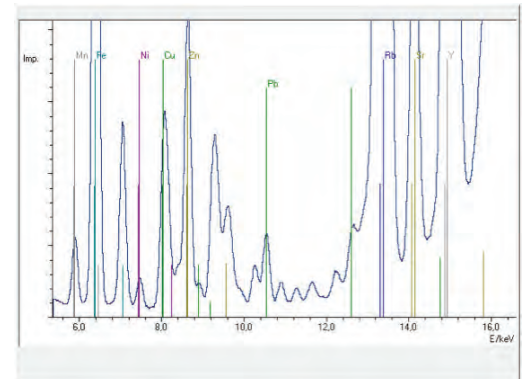


Figure 3: Examples for artifacts in the measured spectrum, logarithmic scale

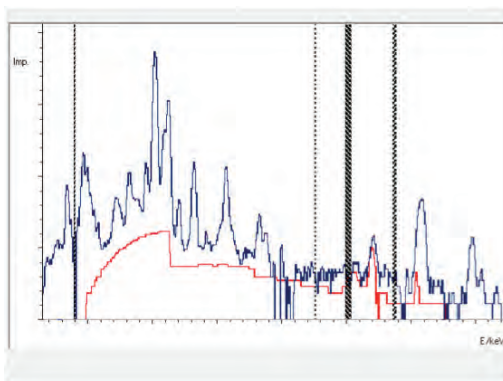
- Shelf and Tailing, mainly caused by escape of electrons from the detector at the detector surface
- Escape of Si K X-rays from the detector
- Pileup and Continuous pileup caused by the limited time resolution of the spectrometer

All of the above-listed effects must be corrected for, prior to or during the deconvolution of the spectrum.

In the case of polychromatic excitation, for example, fitting the background requires consideration of any scattered radiation. This radiation contributes to the background spectrum and can be partially absorbed by the elements in the sample. The absorption edges must be taken into account for background subtraction (Figure 4).

Especially in the high-energy region of the spectrum, fluorescence radiation can also be Compton-scattered, depending on the composition or the average matrix of the sample. This effect becomes visible in the spectrum and has to be corrected as well (Figure 5).

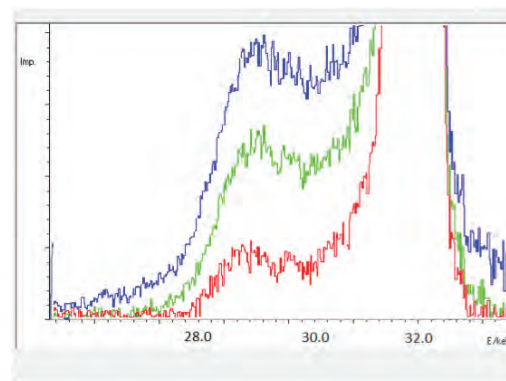
Figure 4: Background fit for a sample spectrum with absorption of the scattered background in logarithmic scale



Deconvolution of the spectrum can be completed once this is done. The possibility of interferences requires fitting fluorescence signals from a complete series — for example, the complete Pb L series — not just signals from one element. With this approach, the use of Pb L- α and As K- α as the element's most sensitive signals is possible although both lines interfere, because the other lines of the series (Pb L- β , L- γ , L-I and As K- β) are not interfering.

When starting the spectrum deconvolution, additional influences — that can be corrected based only on concentration information — must be dealt with. Because a first deconvolution would have already given a good estimation of the net intensities, these can be used to

Figure 5: Spectra from samples containing 2000 mg/kg Ba in 100% SiO₂ (displayed in blue), in 50%/50% SiO₂/CaO (displayed in green) and in 50%/50% SiO₂/Fe₂O₃ (displayed in red) in linear scale



calculate sample concentrations. For a perfect deconvolution, the proportion of the line ratios should not be considered as constant but should be adjusted based on the concentrations of the elements present in the sample. This is because another element in the sample might create an absorption edge that would influence the ratios among the lines of the series.

To correct for these effects, spectra processing is repeated using the sample composition calculated from a first “classical” analysis approach. An extreme example is shown in Figure 6. The K- β /K- α line ratio of the element Fe of sample NOD-P1 (including 29.1% Mn) is significantly different than the ratio in a spectrum from, e.g., a granite sample. This is caused by the strong absorption edge from Mn between the Fe K- α and K- β lines. In contrast to typical absorption phenomena, in this example the K- β line is lower in intensity than

expected (due to the absorption by Mn). As a result of this matrix effect, 2240 $\mu\text{g/g}$ Co are not detected with a classical approach, although the LOD of Co is 2.4 mg/kg (using the Co K- β line) in a pure SiO₂ matrix. All line ratios can be corrected by using the sample composition calculated from the first iteration.

The final proof of a good deconvolution can be performed by calculating the determined net intensities of all elements, creating an artificial spectrum and comparing this to the corrected original spectrum. Good agreement confirms a good quantitative analysis.

Deconvolution software evaluates the raw spectrum including all artifacts and any increased background. For example, it starts by using a spectrum such as the one displayed in Figure 7.

Figure 6: Comparison between measured spectrum (blue) and fitted sum spectrum (red) of pure element spectra (not considering different absorption) in logarithmic scale

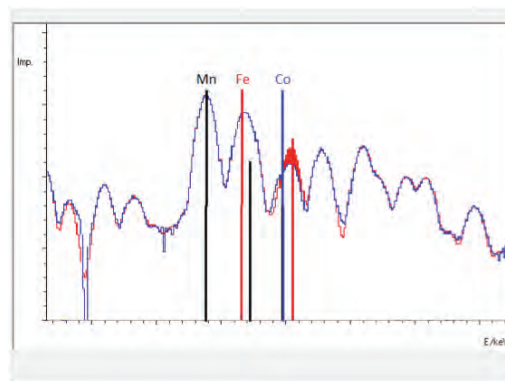


Figure 7: Raw spectrum before corrections and deconvolution in logarithmic scale

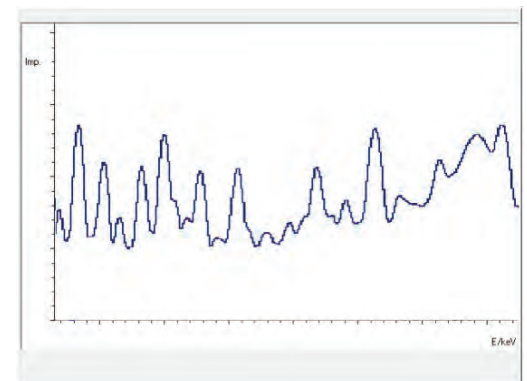
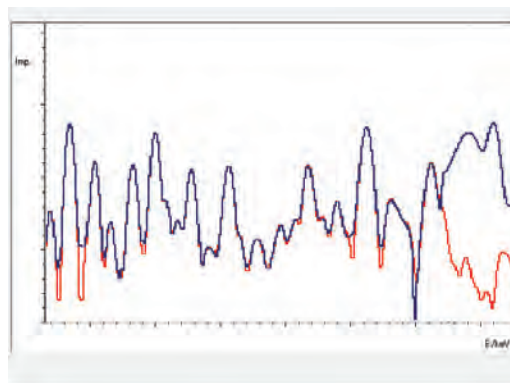


Figure 8 shows the spectrum after the subtraction of the corrections and the background spectrum (displayed in blue) compared to the artificial spectrum that is reconstructed by using the net intensities from the deconvolution (displayed in red). The better the agreement between both spectra, the better the accuracy of the calculated net intensities.

Figure 8: Spectrum after corrections (displayed in blue) and the reconstructed spectrum using the net intensities from the deconvolution (displayed in red) in logarithmic scale



Conclusion

The basis for an accurate analysis of trace, minor and major elements using XRF is the ability to collect and correct fluorescence signals and artifacts in the spectrum. Background spectra that cannot be fitted easily will be especially matrix-dependent. Correcting these effects and performing a proper deconvolution of the net spectra lead to an accurate determination of the net intensities. These then can be used to obtain accurate analysis results utilizing mathematically based matrix-correction algorithms.

To learn more about overcoming the matrix effect, the SPECTRO XRF product line or TURBOQUANT, the SPECTRO solution for rapid analysis of completely unknown matrices, visit

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