

Full Spectrum Modeling: Understanding the Matter

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In the classical approach of the fundamental parameter (FP) method, measured count rates are extracted from the observed spectrum by peak fitting or deconvolution and usually by subtracting the background, which is determined by numerical procedures. The quantification of an unknown sample is performed in an iterative procedure where those measured count rates are compared with computed fluorescence intensities, calculated with analytical equations.

Modern FP based quantification cannot be reduced to the calculation of primary and secondary fluorescence count rates. Instead of evaluating the measured spectrum the analytical calculation is extended by all effects in the detection path including detector and electronic response. Furthermore the calculation of Compton- and Rayleigh scattering of characteristic excitation lines and of continuous Bremsstrahlung, as well, allows the analytical description of the spectral background. Nowadays the simulation no longer ends with a set of fluorescence intensities but with a calculated spectrum, which can be compared to the measured one. The advantage of this extension is the reduction of empirical assumptions, as f.e. a purely numerical background model can be insufficient for trace element analysis. This modern approach allows new quantification strategies and enables the investigation of relevant aspects beyond the pure sample analysis:

- **Mineral identification:** The investigation of mineral samples based on X-ray spectroscopic methods is often done by spectra-match algorithms, where the individual point spectra of a micro-XRF map are compared to reference measurements of pure mineral standards. This very efficient analysis usually requires a large set of reference measurements, acquired with the correct spectrometer configuration. Full spectrum modeling offers the possibility to perform an FP-based spectra-match analysis without reference measurements.
- **Fundamental parameter improvement:** The knowledge of the atomic fundamental parameters (FP) becomes increasingly important and the need for an improvement of the existing databases is well known. Whereas most of these FPs need to be determined at large facilities like synchrotron radiation sources, other parameters, however, are seemingly addressable with table-top instrumentation. Using the atomic line ratios as fit parameter in a calculation based on full spectra modeling we could improve the quality of these parameters and observe a significant decrease of the lower limit of quantification for particular element combinations.
- **Uncertainty estimations:** The uncertainty estimation of analytical results obtained by FP quantification is a challenging task. Most FP databases do not contain any information about the uncertainties of the values. Furthermore simple error propagation calculations are nearly impossible especially in case of polychromatic excitation. However, full spectrum modeling allows investigating the influence of various FP parameters on the simulated spectra and on the analytical results.