

An internally consistent self-calibration approach to fundamental parameter x-ray fluorescence analyses

T. Papp, J.A. Maxwell

Introduction

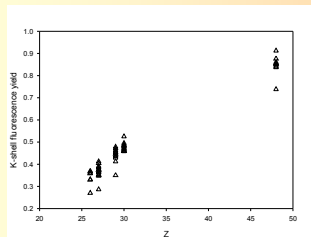
Cambridge Scientific provides an XRF Analyses program (CSXRF) based on a hybrid fundamental parameter approach. It is a truly fundamental parameter approach, with additional options for supplementing unknown basic physical parameters, and equipment information.

The fundamental parameter method is using the fundamental parameters to calculate a model spectrum that best represent the measured spectrum.

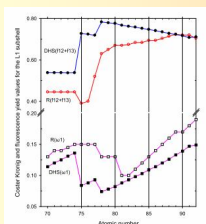
However, some of the fundamental physics parameters are purely known, and the equipment details are absolutely important, and frequently not well specified. The hybrid FP approach uses FP to define a model spectrum that is fit to the data to provide element peak areas. Measurements on known standards, allow to specify the detector efficiency, the absorbers' thicknesses, and fine tune the excitation function at the sample position - thus the hybrid approach. If CSX signal processors are used for the measurements, it also evaluates the rejected events spectra, to derive the true input rate for each x-ray lines in the spectrum.

Some features: Lorentzian line shape, x-ray satellites, parameterized detector tailing, secondary- and tertiary fluorescence, layered sample, unknown matrix correction, visible and invisible elements, coatings..

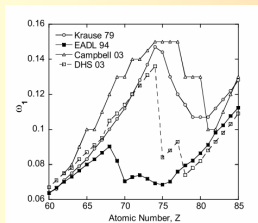
The inconsistencies and unreliability of the basic atomic parameters [1,2], as well as the inaccuracies of the precise description of the equipment parameters, demand a daunting task in applying the fundamental parameter (FP) approach in x-ray analysis. Below we present some examples for the level of knowledge of basic parameters.



The experimental K_K-shell fluorescence data measured in the last ten years. The standard FP method would not work in all these laboratories, as they have different level of understanding what they are doing, otherwise better results with less scatter would be achieved. In this case the additional options offered by our hybrid method, could help, to adjust for the unknown, like limited knowledge of detection or excitation details.

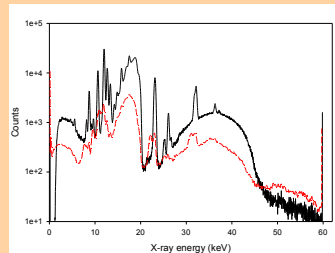


Comparison of the experimental and theoretical L1 subshell fluorescence yield and Coster-Kronig transition probabilities. The experimental data is internally inconsistent in an extent of more than 100%. http://www.atomki.hu/ar2005/3_atom_nol/a07.pdf

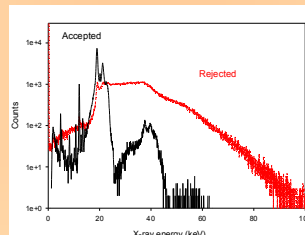


Comparison of various compilations. From [2], with permission.

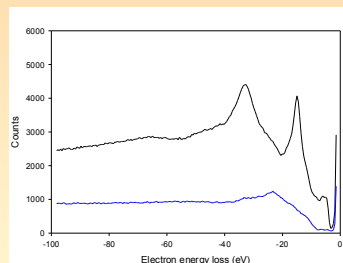
With a quality assurance capable signal processor [3,4], we have overcome the limitations of the signal processing approaches clearly described by Dr. P Statham [5], and the detection arm can be properly handled, even at very high input rates. The proper knowledge for the electronic efficiency in varying noise environment is crucial. It is solved via analyzing the rejected events spectra as well, accounting for all events.



An XRF spectrum of an ABS sample measured on a portable XRF device. The rejected spectrum is also shown with dashed line.



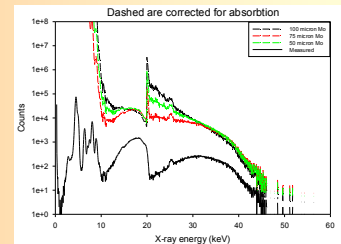
An XRF spectrum of a thick polyethylene sample measured on an industrial XRF system for a 30 seconds measuring time. The accepted spectrum (continuous line) has a good resolution and a small visible pile up in the 36-45 keV range. The rejected spectrum is also presented (dashed line). It readily presents that the count rate was very high, resulting in a large number of pile ups, indicating that smaller beam current would be optimal.



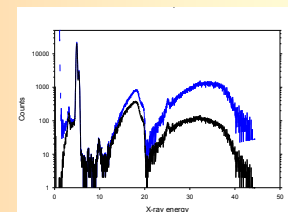
Additional care need to be taken at layered targets, with the secondary electron ionisation cross sections, because in different chemical forms it may have a huge change. The above figure gives an example, presenting an electron energy loss measurement.

The other arm is the excitation arm at XRF equipment. It is crucial to know the x-ray spectrum at the sample position, which will make the excitation. It demands, the precise knowledge of the x-ray tube function, the absorbers and the geometry. Usually the x-ray tube function is purely known and difficult to determine experimentally.

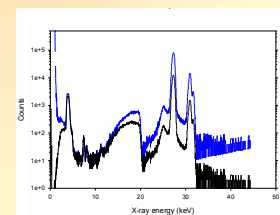
We have developed a user friendly approach, where an inverse FP method is used to determine the synthetic tube function at the sample position, from a multi-element standard spectrum. This method will accommodate the inconsistencies and inaccuracies of the basic physics parameters in first order. However, the inaccuracies in the atomic parameters will not be sufficiently compensated with layered targets, and will give limitations in the layer accuracy.



A spectra measured with an industrial XRF machine. Absorption correction for the prefilter was used to determine the prefilter thickness. The assumed thickness was not the same as the x-ray absorption thickness.



The scattered spectrum in the measured spectrum is used to justify that the selected tube function is suitable for the application. Scattering on a low Z element has mainly Compton scattered events beside the Rayleigh scattered. The black line is the measured, while the blue is detector efficiency corrected spectra.



Measured spectrum on a high Z element, where the Rayleigh scatter dominates. Since the scattering has polarization dependence, and the x-rays from the x-ray tube are generally polarised, care should be taken on the potentiality of polarisations.

Conclusions

The high quality truly fundamental parameter method needed to be amended with services where the knowledge of basic physical parameters, and equipment descriptions are limited or inaccurate. The CSXRF FP software were supplemented with an inverse FP method, which allow to derive the unknown physical parameter or equipment parameters, in a synthetic way, that the measurements on a set of standards are best represented. The more information is supplied the best results are achieved. We consider it as a hybrid method. There are many resonance type features in various measurements, and such a method is very necessary in such cases. On several classes of materials the method were tested in industrial environments, including RoHS, gold, plastic, coating thicknesses, e.t.c.

References

- [1] T. Papp, X-Ray Spectrom. 41, (2012) 128 – 132
- [2] Y. Namito, S. Ban, H. Hirayama, Physical Review A 2008, 78, 033419
- [3] T. Papp, and J.A. Maxwell, Nucl. Instr. and Meth. in Phys. Res. A 619, (2010), 89
- [4] T. Papp, J. A. Maxwell and A.T. Papp, Spectrochimica Acta Part B 64 (2009)761
- [5] P. J. Statham, X-Ray Spectrometry Vol6 No2 (1977) p.94;