

1 Quantitative XRF Analysis using Fundamental Parameters

1.1 Purpose of XRF Analysis using FP

In simple terms, the purpose of XRF analysis with FP is to convert elemental peak intensities to elemental concentrations and/or film thicknesses. This is achieved typically through a calibration step, where the XRF response function (related to parameters that are independent of the sample matrix) for each element is measured using a known standard of some kind. In some circumstances the analysis may be purely based upon theoretical equations, and the fundamental-parameter database, without any need for a calibration step. The latter is possible for analyses of simple bulk or single-layer thin-film samples, when the film thickness is known (e.g., a bulk sample).

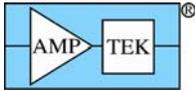
1.2 Overview of FP Analysis

As outlined above, there are only two steps in XRF analysis, whether or not the FP method is used. The first step is to calibrate the response function for each element from one or many standards (called the “Calibration” step). The second step is to produce the sample analysis of a given material, using the previously stored calibration coefficients, and the FP algorithms given a definition of the sample (i.e., number of layers, and which elements are in which layers).

The FP32.dll library will support single layer or bulk composition and thickness analysis of up to 30 elements, calculated as either elements and/or compounds. Up to 4 or more excitation “conditions” are allowed per analysis. Each condition describes a separate analysis, and can be freely defined with any combination of experimental conditions, such as kV, tube anode, filter, detector filter, environment (air, vacuum, He) and acquire time. This allows the analyst to measure some elements with one condition, and others completely differently, such that each analysis can be optimized for the specific element, or group of elements. Likewise, the spectrum processing steps can also be freely defined, and are all part of the so-called condition code setup.

The FP analysis software will support a single or multiple standard calibration scheme, or completely standardless analysis if the tube, detector, environmental and geometry parameters are known. Calibration standards should be passed one at a time and the merging of the calibration standard information is handled internally. After each calibration step, a set of calibration coefficients and associated information, for each of the defined elements, is returned, which can immediately be used if only one standard is employed. When using multiple calibration standards, all the coefficients are merged into one set, and then this final set is available for subsequent quantitative analysis.

The layer thicknesses must be fixed for standardless analysis. Results can be normalized to any value, and MUST be normalized for standardless analysis or when the layer thicknesses are calculated. Elements (or compounds) can be calculated, fixed, or determined by difference. Elements can also be determined by stoichiometry from the compound formulae. Composition results can be calculated in units of Wt% or ppm, and for thin films, units such as $\mu\text{g}/\text{cm}^2$ and mg/cm^2 are used for mass thickness. The latter can be converted to thickness (microns, microinches, nm, etc.) if the density is known. The density may be input or optionally calculated theoretically.



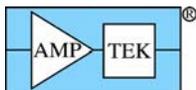
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All the appropriate FP calculations are made both during calibration and for Quantitation, using calculations based upon the Sherman equation. Tube spectra, required for the direct fluorescence calculations, can be supplied by the user, or calculated from built-in models (Ebel, Pella et al.). These tube spectra can be convolved with experimental transfer functions to derive the expected tube spectrum passing through an optic such as a polycapillary bundle. The presence of air paths will also be calculated from the input geometry parameters, for both the source and detector paths. Single-element filters can also be inserted between the tube and the sample, or between the sample and the detector, and the software can accommodate both.

The detector parameters (window, thickness, etc.) will also be used to calculate the various absorption and efficiency effects when x rays pass through the window and get deposited in the detector material. This is only strictly necessary when doing standardless analysis, but the calculations are always done this way for consistency, and to make it easier to compare calibration coefficients between elements. If the theory were perfect, all the calibration coefficients would have the same value. In practice, differences should be relatively small, especially in comparison with coefficients that did not fully compensate for the detector efficiencies. Usually when calibrating elements that all use the same line series (e.g., K), the coefficient variation is small (< 30%), but is often larger when calibrating from mixed lines (e.g., K and L) because it is difficult to make absolute calculations that include the line series information (e.g., fluorescence yields).

It is not necessary to collect pure-element spectra for FP analysis, as no direct ratioing is necessary for the elemental intensities. The calculations are done this way to make it easier to do standardless analysis. Of course, it is possible to use pure-element standards if desired, and the complete FP calibration may be done this way, without any “type” standards being used at all. This is useful if the analyst does not have type standards readily available.

Both direct and secondary fluorescence effects are considered in the FP calculations. Included in the FP database are all the required parameters to calculate or recall absorption coefficients, fluorescence yields, jump factors, Coster-Kronig transitions, line energies, line ratios, etc.



1.3 Selected References for the FP Method and Databases

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- (c) "Handbook of X-Ray Spectrometry: Methods and Techniques," eds. R.E. van Grieken and A.A. Markowicz, Marcel Dekker, Inc., New York (1993).
- (d) "An Analytical Algorithm for Calculation of Spectral Distributions of X-Ray Tubes for Quantitative X-Ray Fluorescence Analysis," P.A. Pella, L. Feng and J.A. Small, *X-Ray Spectrometry* 14 (3), 125-135 (1985).
- (e) "Addition of M- and L-Series Lines to NIST Algorithm for Calculation of X-Ray Tube Output Spectral Distributions," P.A. Pella, L. Feng and J.A. Small, *X-Ray Spectrometry* 20, 109-110 (1991).
- (f) "Quantification of Continuous and Characteristic Tube Spectra for Fundamental Parameter Analysis," H. Ebel, M.F. Ebel, J. Wernisch, Ch. Poehn and H. Wiederschwinger, *X-Ray Spectrometry* 18, 89-100 (1989).
- (g) "An Algorithm for the Description of White and Characteristic Tube Spectra ($11 \leq Z \leq 83$, $10\text{keV} \leq E_0 \leq 50\text{keV}$)," H. Ebel, H. Wiederschwinger and J. Wernisch, *Advances in X-Ray Analysis*, 35, 721-726 (1992).
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- (i) "Comparison of Various Descriptions of X-Ray Tube Spectra," B. Schoßmann, H. Wiederschwinger, H. Ebel and J. Wernisch, *Advances in X-Ray Analysis*, 39, 127-135 (1992).
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- (k) "Calculation of X-ray Fluorescence Cross Sections for K and L Shells," M.O. Krause, E.Ricci, C.J. Sparks and C.W. Nestor, *Adv. X-ray Analysis*, 21, 119 (1978).
- (l) X-Ray Data Booklet, 2nd Edition, Lawrence Berkeley National Laboratory, eds. A.C. Thompson and D. Vaughan, LBL, University of California, Berkeley, CA 94720 (2001).
- (m) "Revised Tables of Mass Attenuation Coefficients," Corporation Scientifique Claisse Inc., 7, 1301 (1977).
- (n) "Atomic Radiative and Radiationless Yields for K and L shells," M.O. Krause, *J. Phys. Chem. Reference Data* 8(2), 307-327 (1979).