



SPECTROLAB

Oxford House, 20 Oxford St. Newbury, Berkshire. RG14 1JB UK. Offices in UK, EU, Dubai
sales@spectrolab.eu sales@spectrolab.co.uk www.spectrolab.co.uk **CAT711006**

X-Ray Fluorescence

Spectroscopy

EDXRF 9000E Fundamental

Parameter software for EDXRF

without standards

Version 3.0
Safety class 1 (EN 61010-1)



Image shows the model 9000 EDX

6

Instrument FPC Software Fundamental Parameter Calibration

Application - Introduction

1. Introduction

Recently innovations in X-ray fluorescence spectroscopy were related to both hardware and software improvements. This section of the manual does not aim at describing hardware innovations but is confined to analytical software. The main item is the route “from precision to accuracy”. In other words, what are the limitations to the accuracy of the analytical result if the fluorescence intensities can be determined with high precision?

The above question, which relates to the keyword “calibration”, cannot be answered in a simple way. In this section the main focus will be on fundamental parameter based quantification and some remarks will be made on influence coefficient based calibration and quantification. Both methods start from the same equation which describes the production of X-rays in a sample when irradiated with an X-ray beam. In general, the following properties of such influence coefficient methods might seem relevant:

1. Influence coefficient methods aim at the transformation of non-linear equations into a set of linear ones. A consequence is the conversion of integration over many wavelengths into evaluation at a single, effective, excitation wavelength.
2. The models incorporate effects of third elements by introduction of either more coefficients or by performing a calibration in various concentration ranges.
3. Influence coefficient methods only work when all elements in the sample have been accounted for in the calibration.
4. In practice a series of “type standards” are required to do a calibration. This means that the procedure is fit for process control, but not for analysis of completely unknown samples.
5. The influence coefficient models are only operational for bulk materials and are not suitable for layered samples.

The Instrument FP program employed is based in the Htek FP32. Program dll software. The core algorithm of the FP program is the same as with the Spectrace (Thermo) and CMI (Oxford instruments). The key point of FP calculation is to obtain the net intensity of each element in the sample. As long as the correct net intensity of each element is inputted correctly into the program, satisfactory results can be calculated by the FP software

2. FP Application

(1) Definition

The "fundamental parameters" approach to calibration in X-ray fluorescence spectroscopy is unique because it is based upon the theoretical relationship between measured X-ray intensities and the concentrations of elements in the sample.

This theoretical relationship is based upon standard X-ray physics and the measured values of fundamental atomic parameters in the X-ray region of the electromagnetic spectrum. Chemical matrix effects can occur as X-ray absorption and enhancement phenomena. The presence of certain metals can interfere with the analysis of certain other metals. For example, iron tends to absorb copper X-rays, whereas chromium levels will be enhanced in the presence of Iron. These effects can be corrected mathematically through the XRF instrument's FP software.

(2) Advantages and introduction of the FP program

- Up to 30 elements can be analyzed at a time. Analysis can be performed for all elements from Na through U, using K, L or M lines.

The screenshot shows the 'Edit elements' window with a table of parameters for various elements. The table has the following columns: Element, Lines, Peak(L), Peak(R), Peak/Bkg, Base Method, Bkg(L), Bkg(R), Difference, Intensity method, and Fitting element. The data rows are as follows:

Element	Lines	Peak(L)	Peak(R)	Peak/Bkg	Base Method	Bkg(L)	Bkg(R)	Difference	Intensity method	Fitting element
Ag	Ka	2175	2259	<input checked="" type="checkbox"/>	Full area	50	4046	<input checked="" type="checkbox"/>	FP Gaussian f...	
Ti	Ka	423	475	<input type="checkbox"/>	Full area	50	4046	<input type="checkbox"/>	FP Gaussian f...	
Fe	Ka	616	668	<input type="checkbox"/>	Full area	50	4046	<input type="checkbox"/>	FP Gaussian f...	
Ni	Ka	717	776	<input type="checkbox"/>	Full area	50	4046	<input type="checkbox"/>	FP Gaussian f...	
Cu	Ka	778	834	<input type="checkbox"/>	Full area	50	4046	<input type="checkbox"/>	FP Gaussian f...	
Zn	Ka	840	891	<input type="checkbox"/>	Full area	50	4046	<input type="checkbox"/>	FP Gaussian f...	
V	Ka	476	521	<input type="checkbox"/>	Full area	50	4046	<input type="checkbox"/>	FP Gaussian f...	

Below the table is a summary section with the following fields:

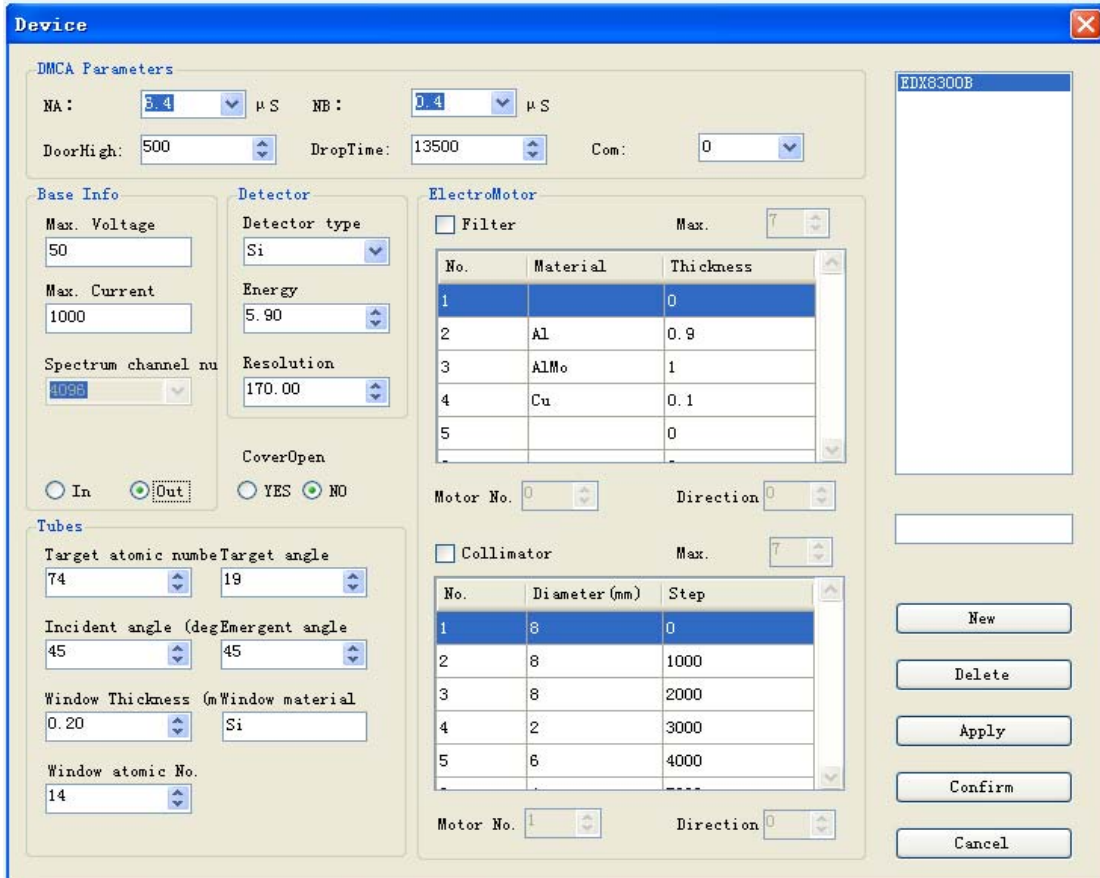
Main Element	Fitting element	Fitting(L)	Fitting(R)	Bkg(L)	Bkg(R)	Peak/Bkg

At the bottom of the window, there are several controls:

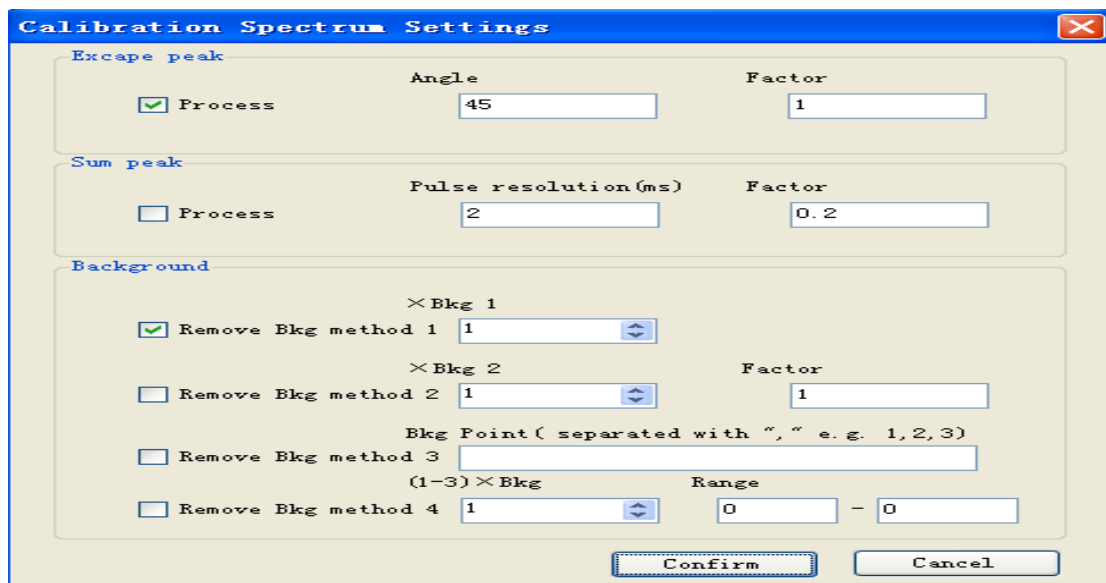
- Normalized: 99.990
- RhThickness: 0
- Alert

Buttons at the bottom include: Add, Delete, Up, Down, Apply, Confirm, Cancel, Previous, Next.

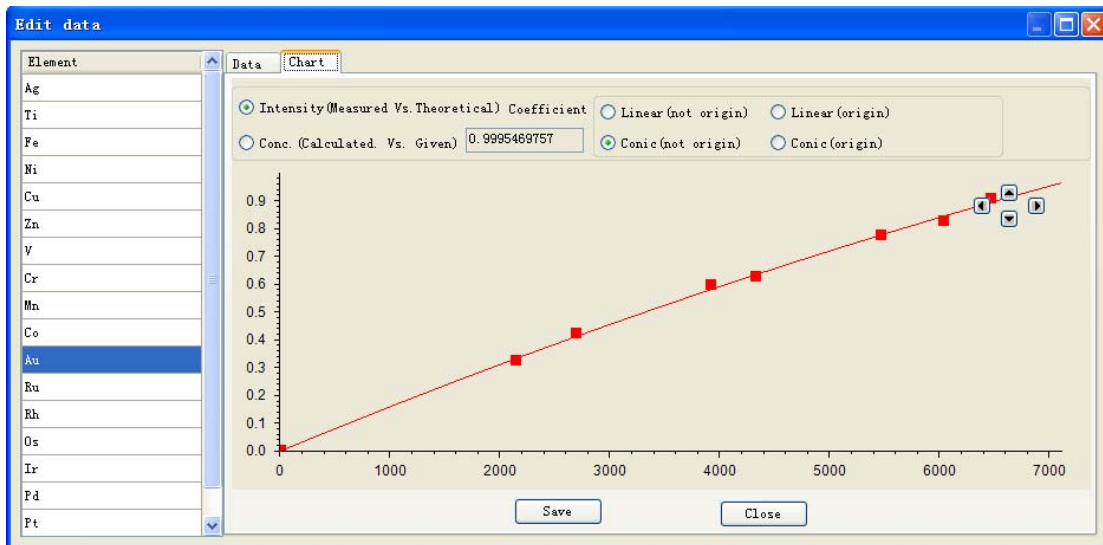
Supports measurement of bulk composition, composition and thickness of a single layer, or composition of up to 5 layers. Includes full correction for losses due to attenuation in air, detector Be windows, detector dead band, the detector's active volume, and filters inserted between the tube and sample or between the sample and detector. These are calculated from the user – input parameters defining the excitation source, the detector, and the spectrometer geometry.



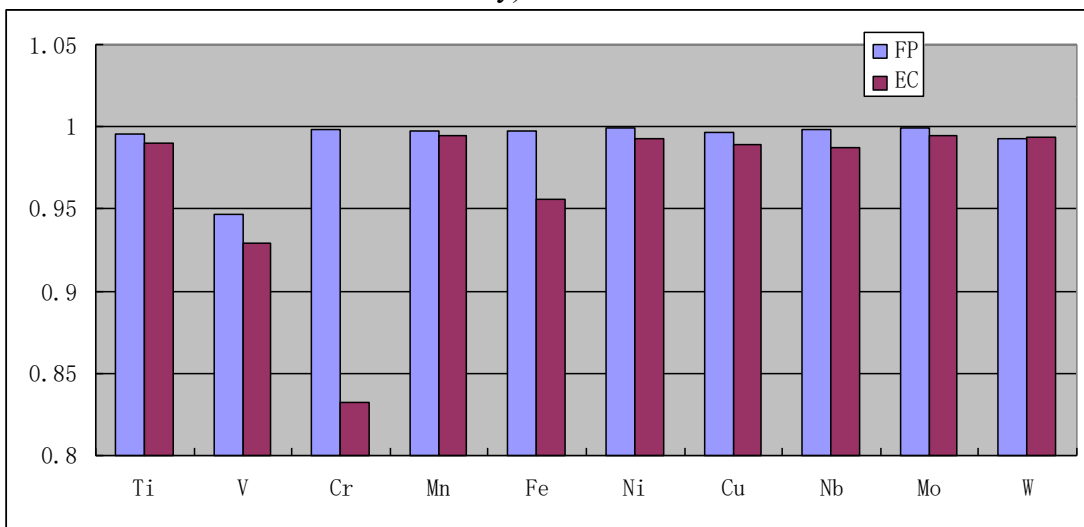
Spectrum processing parameters include quantities to define the background continuum, pile-up and some peaks smoothing, and a measured background spectrum for peaks.



3.

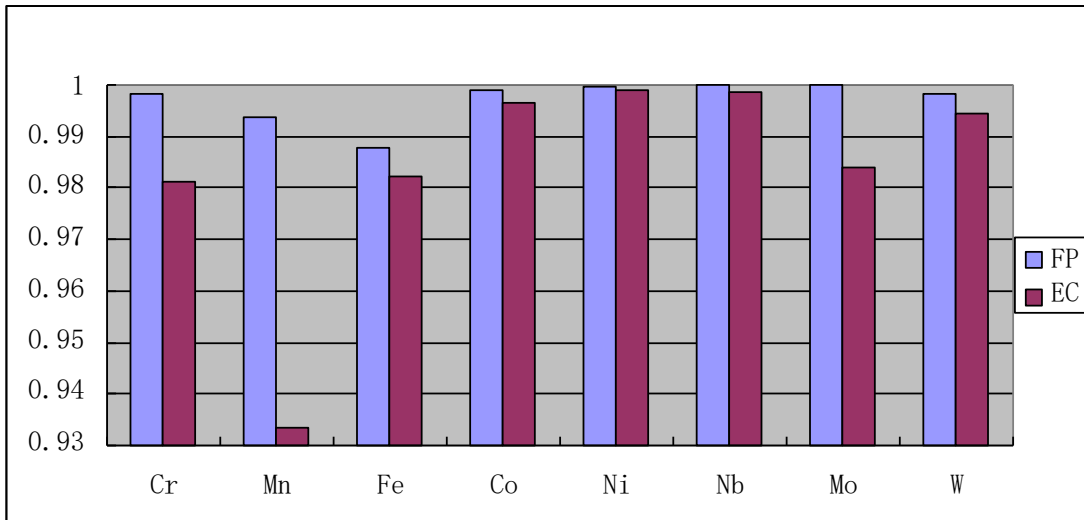


Graph below shows the FP calibration curve of **Ag**. (Y axis is the theoretical intensity and the X axis is the measured intensity)



3) Cobalt alloy

By applying the same standards (16 cobalt alloy standard samples are inputted) for calibration Compare the linear coefficient of the calibration curve between EC and FP. (The closer to 1 of the coefficient ,the better linearity of the curve)



4. Factors that can compromise the quality of FP results

(1) Sample Matrix effects

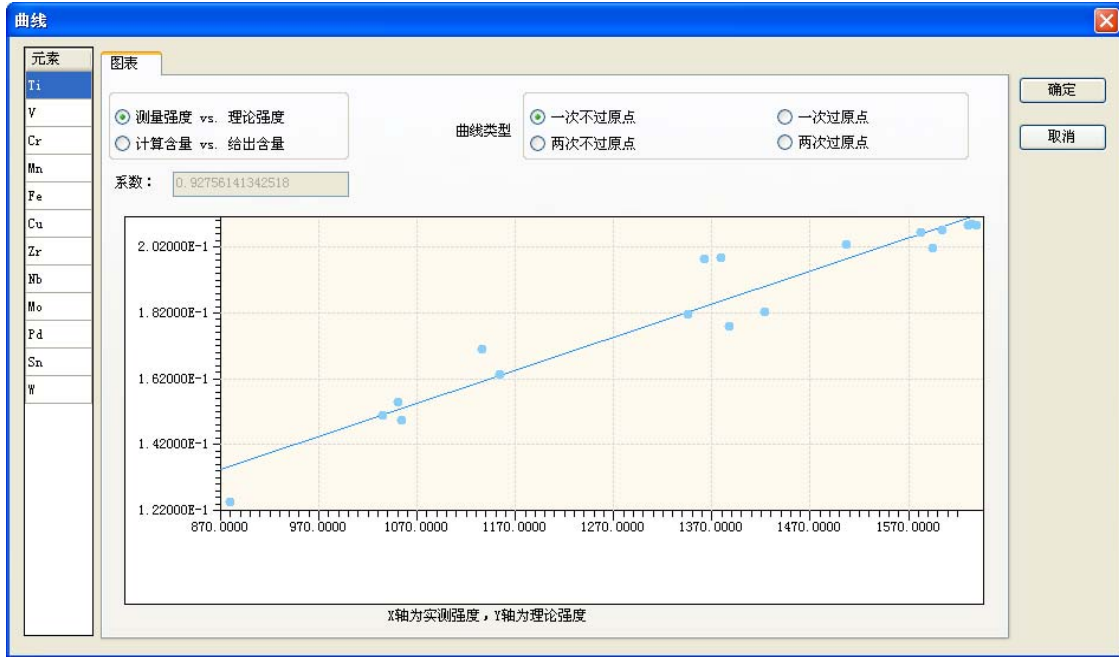
Sample matrix effects include particle size, uniformity, homogeneity, and condition of the sample surface. Every effort should be made to homogenize samples thoroughly before analysis. One way to reduce particle size effects is to sieve all powder type samples including minerals or soil before analysis is made

Inconsistent positioning of samples in front of the detector window is a potential source of error because the X-ray signal decreases as the distance from the X-ray source increases. Maintaining a consistent distance between the window and the sample minimizes this problem. For best results, the window of the detector should be in direct contact with the sample.

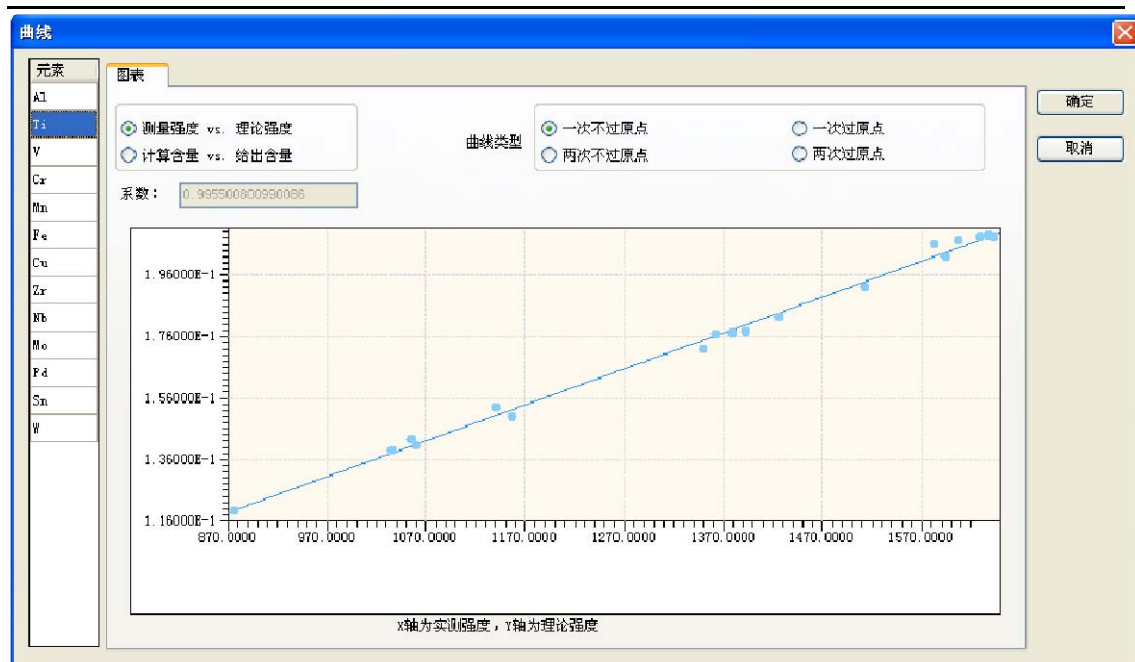
Total concentration of the target elements must be 100%. If something is missed, the final test result will be incorrect .

For example:

Take the Titanium sample for example. 18 Titanium standards are used for calibration. All of the standard samples contain from 1-7% Aluminum inside. Under the same test conditions, the first calibration didn't take the aluminum into its calculation but the second calibration did.



Graph above: Calibration without Aluminum. The Y axis is the theoretical intensity while the X axis is the measured intensity



Graph above: Calibration with Aluminum. The Y axis is the theoretical intensity while the X axis is the measured intensity.

Instrument parameters

Hardware parameter factors:

Instrument resolution limitations may cause problems in analyzing some elements. If the energy difference between the characteristic X-rays of two elements (as measured in eV) is less than the resolution of the detector in eVs, then the detector will not be able to resolve the peaks. In other words if two peaks are 240 eVs apart, but the resolution of the detector is 270 eV, the detector will have difficulty in differentiating those peaks. A common example is the overlap of the arsenic K peak with the lead L peak. With the use of mathematical corrections that subtract the lead interference, lead can be measured from the lead L peak and Arsenic can be measured from the Arsenic K peak. However, concentrations of Arsenic cannot be calculated efficiently for samples that have lead-to-arsenic ratios of 10 to 1 or more, because the lead peak will overwhelm the Arsenic peak completely

Detector Deadtime.

Different CPS (counts per second) can cause intensity loss.

Count rate effects.

The dynamic CPS range of the detector will determine the overall intensity and linearity. The resolution and peak position will also be influenced by this parameter.

Sum peak and escape peak

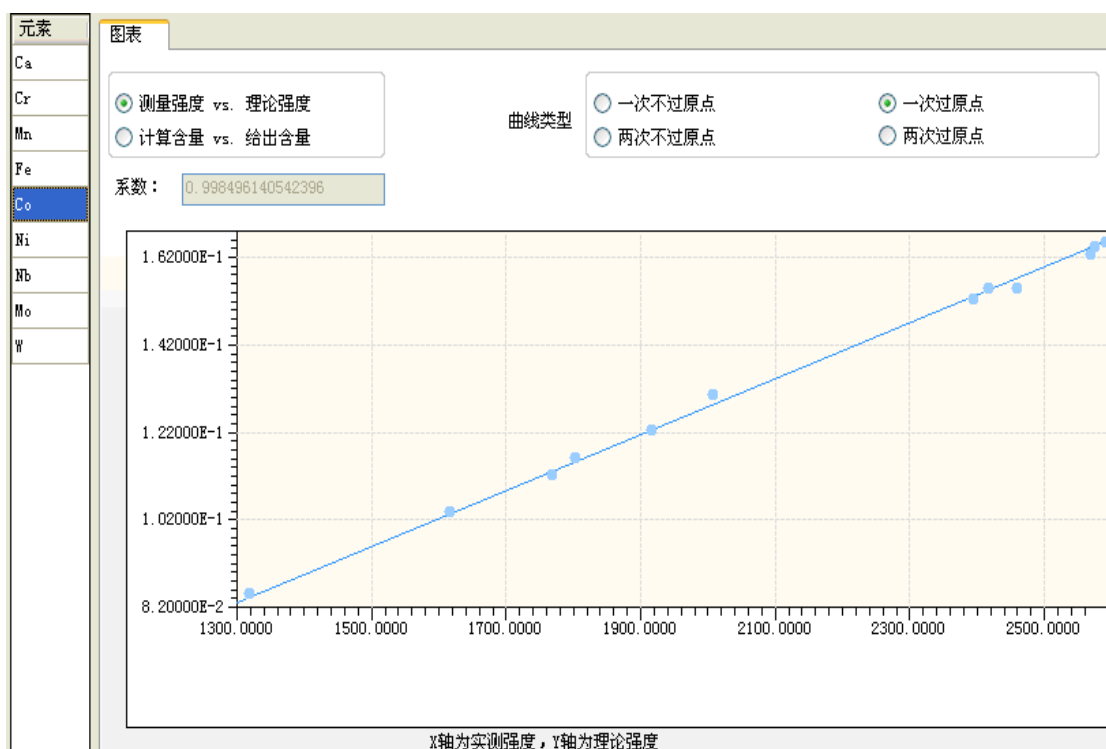
Scattered Background

For example: The peak interference

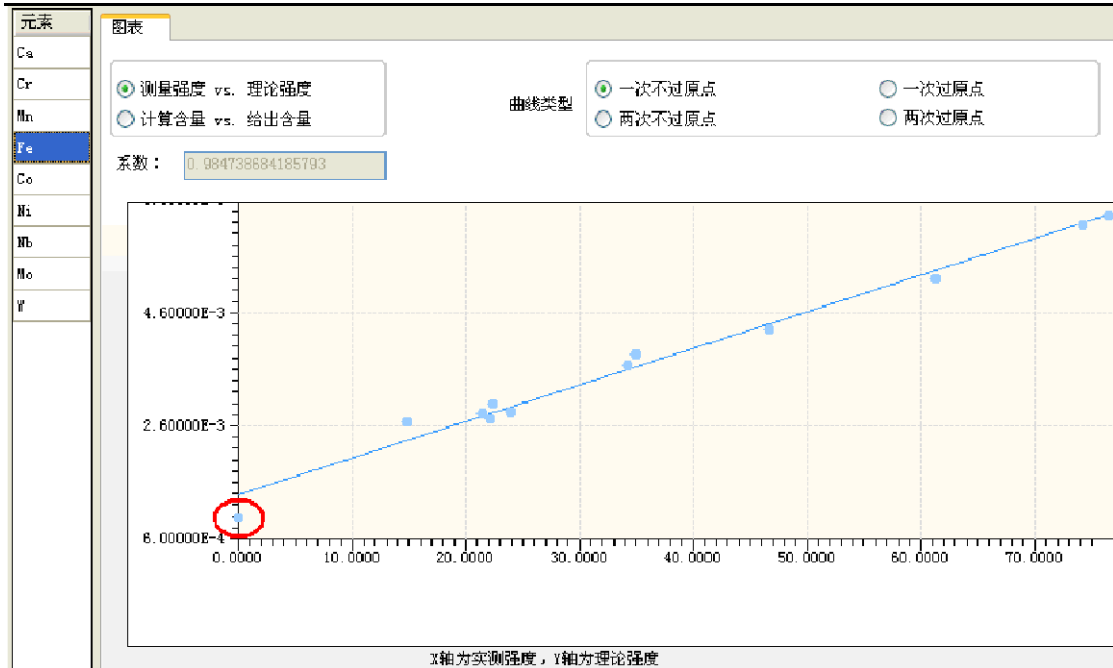
Take Cobalt alloys for example. The pure Cobalt spectrum interferes with the iron peak. In the graph below, the first curve shows the Fe calibration without Co Fitting.

The second curve shows the Fe with Co fitting.

Graph below is the calibration for Fe without Co fitting. (Y axis is the theoretical intensity and X axis is the measured intensity)



Graph below is the calibration for Fe with Co fitting. (Y axis is the theoretical intensity and X axis is the measured intensity)



(3) Spectrum processing

>Spectrum Calibration

Using known peaks in the spectrum, the software calculates the effective gain (eV/channel) and offset (zero shift) for the spectrometer. These factors are applied to subsequent spectra prior to their spectrum processing.

>Background Removal and Blank Subtraction

The background removal module uses iterative filtering to distinguish peaks, leaving behind the smoothly varying spectral background. This background is then removed from the original spectrum, leaving the peaks.

The blank subtraction module is used to remove peaks due to environmental interference or contamination. These peaks are not due to material in the sample but are in the spectrometer, for example Ar in the air or Al in the filters or Pb in shielding. This module subtracts a spectrum acquired from a "blank" reference material, i.e. one without the elements to be analyzed.

>Escape Peak and Sum Peak Removal

Removes at the user's option both the detectors escape and sum (pile-up) peaks. The escape peak module uses an internal function to estimate the fraction of X-ray events (above the K edge) that will generate K X-Rays that will escape from the front or rear of the detector

>Deconvolution: Intensity Extraction

This module operates on the processed spectrum to extract the net peak intensities for the selected elements. It includes several options. First, the peak areas are computed using one of three methods:(1) simple peak integration across a fixed Region-Of-Interest,

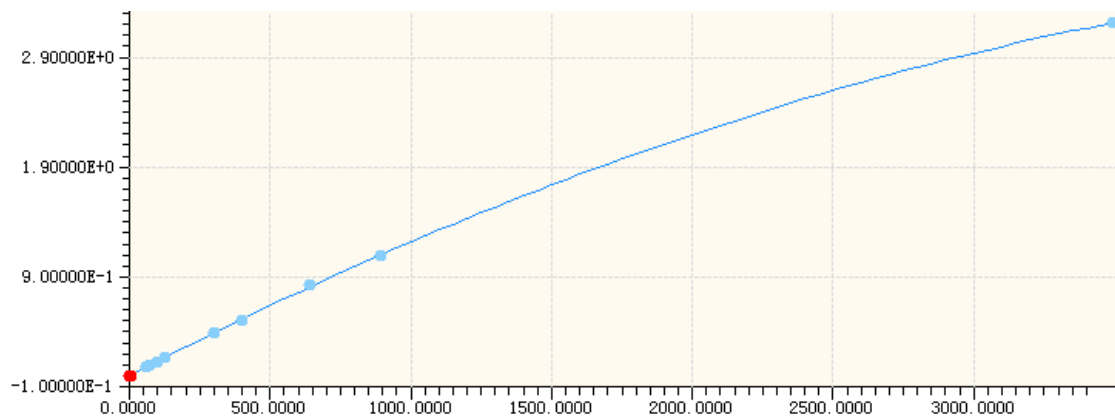
(2) fitting Gaussians to the peaks, using a known database of line ratios and peak energies, etc., and (3) a reference deconvolution, which uses stored profiles for each element to fit the peaks. Second, the spectrum fitting can then be made. All required line energies and resolutions are calculated automatically from the specified analyte line.

(4) FP parameter

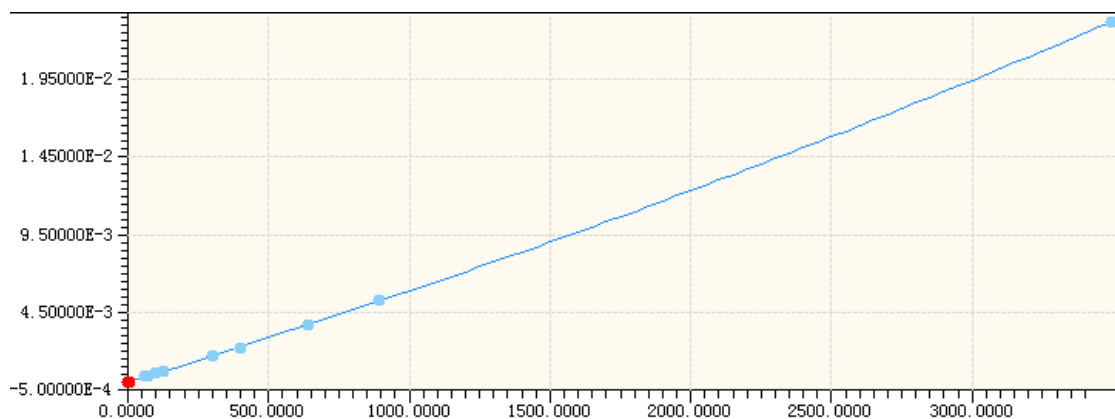
The parameters that influence the theoretical intensity includes: The X-ray tube target material, target take-off angle, tube window material, tube window material, tube incident angle, tube voltage, element energy peak, and filter material

For example, the X-ray tube window material

Y-axis is the theoretical intensity and the X-axis is the measured intensity.
Graph below is the Be tube window material.



Graph below is the Co tube window material



(5) Application details

Many factors need to be considered to reach the net intensity of each element. Factors below need to be carefully used when setting up a new calibration.

1. Adjust count rate during measurement.

Adjusting count rate during a test is designed to remove the influence of the sample shape and instrument hardware differences. When this function is applied to FP calibration, the tube current must be normalized to remove the influence of different test conditions.

2. Sample must fully cover the collimated X-ray beam.

If the sample is not fully covering the collimator beam, the FP program cannot calculate the correct test results.

8 Calibration

. EC- Empirical Coefficient Method

1. EC Application

(1) Definition

EC method is based on the Sherman equation as below:

$$C_i = D + EI_i(1 + \sum_j \alpha_j I_j)$$

(2) Features

Test results are based on standard samples. The more similar standards are with the unknown sample, so the better the results that can be determined.

There are no limits for 100% percent sample measurements

Calibration procedure is easily achieved.

Suited for specific applications

For example, the correction by EC of Fe with Pb

$$C_i = I_j K_{CPS} I_i + D$$

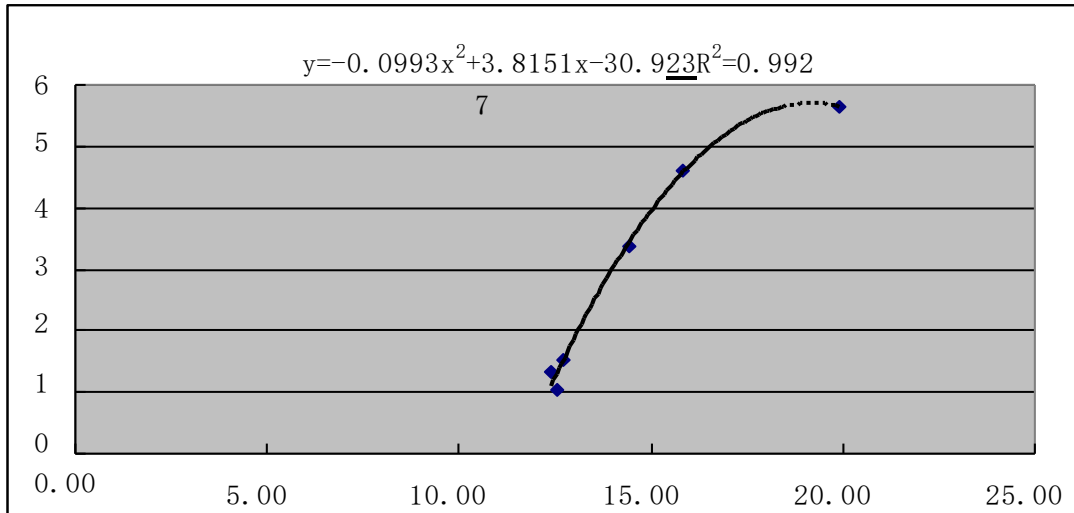
(C_i is Pb content, I_i is Pb intensity, I_j is the Fe intensity, K is CPS coefficient, K needs to be calculated by the EC program)

Application conditions

1) At least 3 standards are needed to build the calibration. 2) Sample surface must be flat, even and homogeneous.

3) Sample bulk should have *infinite* thickness (For XRF concentration analysis)

4)



. The procedure to analyze an unknown sample

1. Obtain a good quality sample;
2. Confirm the target element and content range.
3. Analyze the samples physical condition to see if it needs any sample preparation.
4. Confirm the standards or pure metals needed for measurement;
5. Confirm which calibration mode is the best for the application
6. Apply the optimized test condition: Tube voltage and current , collimator size and filter etc.
7. Analyze standard and sample . Insure that the sample fully covers the collimator beam
8. Choose the best method for spectrum processing and obtain the correct net intensity of each element
9. Create the calibration curve
10. 10 Test sample and generate a test report. A Standard Gold test report is as follow

. Customized test reports are optional.

9

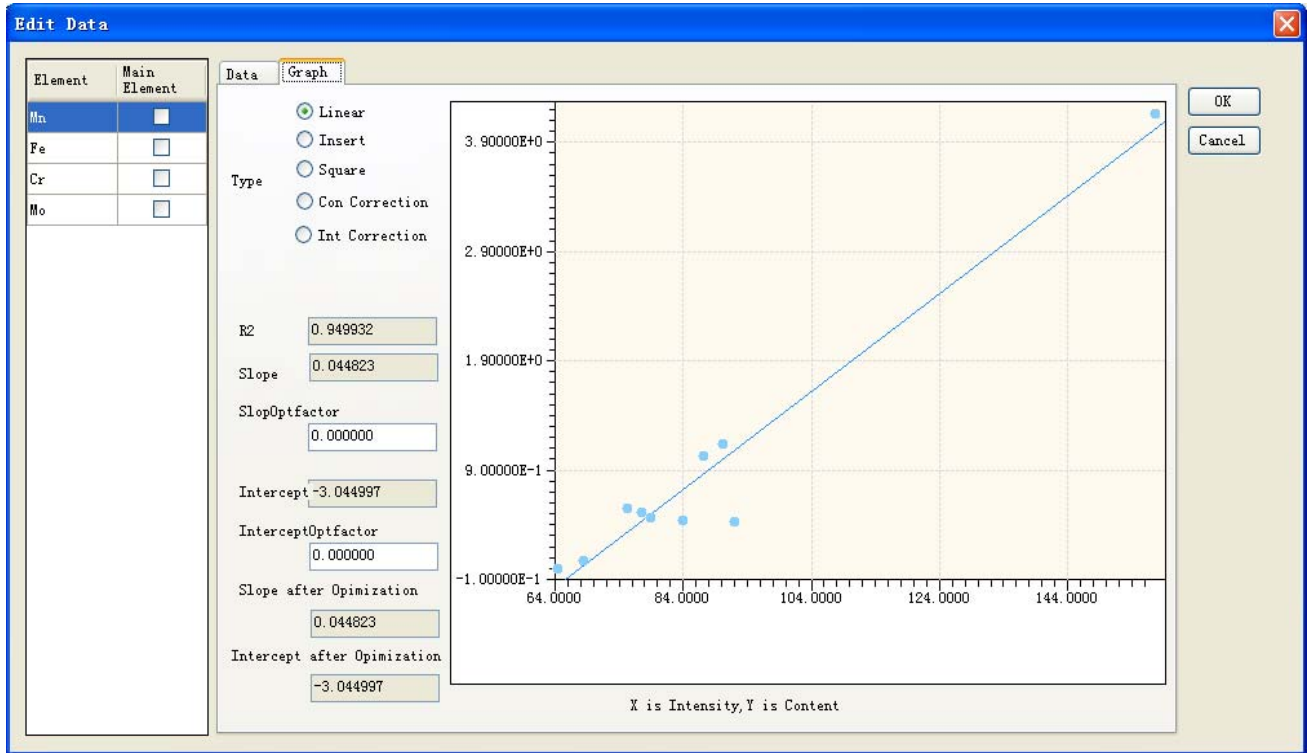
Interferences

(2) Mn influenced by Cr and Fe in alloy analysis

Database is as below:

Sample	Mncps	%Mn	Fecps	%Fe	Cr cps	%Cr
PureFe	64.4	0	2856	100	28.1	0
IARN35D	77.4	0.52	2595		62.5	1.19
BS46	79	0.47	2447	95.5	88.5	2.23
BS47A	84	0.44	2273	94.1	144.7	4.22
BS48A	92.1	0.43	1811	88.52	240	8.75
<hr/>						
15252	87.2	1.03	2608	94.7	51.4	0.75
FC2	68.5	0.07	2713	98.8	55	1
BS3952	75.3	0.546	2743	97.96	30.6	0.105
13937	90.2	1.14	2768	98.8	34.1	0
13599	157.7	4.16	2733	95.8	29.7	0

For Mn, the graph below shows the intensity against concentration without any correction. (Y axis is the measured intensity and X axis is the certified content)



The graph below shows the Mn curve after applying EC correction.(Y axis is the corrected intensity and X axis is the certified content

