The code for processing of the SRXRF spectra.

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The X-ray fluorescence (XRF) analysis with using synchrotron radiation (SR) is a powerful technique for resolving elemental composition of the different samples with high sensitivity and good special resolution.

For precise quantitative analysis, the procedure for robust and reliable processing of the XRF spectra is necessary. Especially, such code is very important for realization scanning mode of the XRF analysis for the operative treatment big spectral data.

As a rule, the specialized codes for conventional XRF systems are not suitable for this aim because of the SR excitation provides a big variety of the analysis modes. Thus, the proposal of the code for processing of the SRXRF spectra is very actual.

The modern program libraries provide a simple ways for organizing robust fitting XRF peaks with keeping a prior data for X-ray lines. In current work, the reliable code for estimation of the XRF peaks areas was proposed. Algorithm suitable for calculation net areas of the peaks in the case of series overlapping and in case violation of the mutual intensity ratios of the line in the series due to sample absorption and due to difference in the registration efficiency.

Code was tested in the new beamline for hard XRF analysis was supported by RFBR grant 17-29-05016 офи_м.

Introduction

The Energy dispersive X-ray fluorescence (XRF) analysis is powerful nondestructive technique for investigation of the element composition inside different samples. The method has a good sensitivity big set of the elements and permits to measure concentrations of the many elements simultaneously. Using synchrotron radiation (SR) for excitation fluorescence dramatically improve the classical XRF analysis capabilities due to possibilities for reduction of the background from scattered primary photons, this become possible , and due to the possibility for choice of the energy of the exited photons.

For proper quantitative analysis of the XRF spectra, the special computer code is necessary. The main approach for such type processing had been described in Van Espen article [1]. Many commercially available devices for XRF have an embedded soft for processing.

However, this software rather can not be used for processing SRXRF spectra. The main reason is a wide diversity of the operational mode for using XRF with SR. Moreover, the using SR possibility to reduce the analyzing volume to few μm, the scanning XRF applications permit to obtain the qualitative XRF image of the elemental distribution with good space resolution. As a rule, such analysis require direct spectra processing simultaneously with sample scanning. The spectra processing code should be embedded into the main program for scanning. Thus the necessity for code for processing of the XRF spectra is obvious. The results for attempt to create such code is described in this work.

Processing procedure

XRF spectra have relatively simple structures and can be easy interpreted. As a rule, XRF spectrum is a set of the XRF lines, which belong to in a special series corresponding certain elements. Every line in the spectrum has a Gaussian profile with central energy equal to well-known and tabulated value . Line width is defined by detector energy resolution, which can be approximated with good accuracy. Relative intensities of lines into one series corresponding atomic transition probabilities also have a priory tabulated data. The common factor for all lines belonged to one X-ray series of the certain elements is proportional to the concentration of this element in the sample, thus the fitting of these factors for all analyzed elements is a goal for quantitative spectrum processing.

Such approach for estimation series contribution in the final XRF spectrum make possible to calculate series integral ever in the case of the peaks overlapping problem which really exist in the analysis geological samples.

Of course, during the fitting one have to take into the mind the possible violation of the tabulated relative intensities due to dispersive dependence of XRF absorption inside sample and due to differences in the registration efficiency for different lines in one series. For correct spectrum processing these effects should be taken into account.

Generally, the simulating number of counts in the i-th channel of the simulated spectrum can be expressed by the next way:

$$Sp(i) = \sum_e C_e \, S_e(i) + Bg(i) \tag{1.1}$$

where $Bg(i)$ –background contribution in the *i*-th channel (will be described later), *e* is element index, C_e – value proportional of the concentration of the certain element in the sample, the estimation of these value is a final goal of the proposed fitting procedure, S_e - a series profile for the element *e*, it includes the set of the Gaussian peaks with fixed positions, amplitudes and widths:

$$S_e(i) = \sum_l T_l^{e*} G(E_l^e, i) \tag{1.2}$$

Here T_l^{e*} is a corrected for registration efficiency tabled value of relative intensities of the lines in the element series, l – is index of the line in the element series. Asterisk denotes the corrected value for accounting sample absorption, efficiency of detection and possible changing amplitude due to changing energy resolution for every line. $G(E, i)$ - Gaussian function (*i*-th channel of the spectrum) with central position in the channel with photon energy equal E, E_l^e - the energy of the *l*-th line in the element *e* series. E

$$G(E, i) = \frac{1}{\sqrt{2\pi} \, w(E)} \exp\left(-\frac{1}{2}\left(\frac{E - E_b - g \cdot i}{w(E)}\right)^2\right) \tag{1.3}$$

Here E_b is an energy of the first channel of the spectrum and g is an energy width of the one spectrum channel, function $w(E)$ describes the dependency of the detector resolution from energy of the registered photons. This dependence can be expressed as rms addition of the detector amplifier noises (No) and statistical uncertainty of the number electron-hole pairs in the detector volume during photon registration $\Delta E = \sqrt{N} \cdot gap = E \cdot gap$:

$$w(E) = \sqrt{No^2 + E \cdot gap} \tag{1.4}$$

The corrected tabular value can be estimated for XRF lines in one series with respect to one reference line (with index l_1) by the next way:

$$\frac{T_{l_2}^{e*}}{T_{l_1}^{e*}} = \frac{T_{l_2}^{e}}{T_{l_1}^{e}} \cdot \frac{F\left(E_{l_2}^{e}\right)}{F\left(E_{l_1}^{e}\right)} \cdot \frac{d_{eff}\left(E_0, E_{l_2}^{e}\right)}{d_{eff}\left(E_0, E_{l_1}^{e}\right)} \cdot \frac{w\left(E_{l_1}^{e}\right)}{w\left(E_{l_2}^{e}\right)} \tag{1.5}$$

here T_l^e - tabulated value for the relative intensity of the line with index l in the element series, $F(E)$ is efficiency of the registration of the photons vs. photon energy, $d_{eff}(E_0, E)$ is effective thickness of sample for exit fluorescence photons (with energy E), with accounting the absorption of primary exciting radiation (with photon energy equal E_0). These functions are described in the next formula.

$$F(E) = \exp\left(-\mu_f(\text{E}) \cdot d_f\right)\left(1 - \exp\left(-\mu_c(\text{E}) \cdot d_c\right)\right) \tag{1.6}$$

Here, μ_f and d_f are the lineal absorption coefficient for detector foil, and thickness of the foil, same factor can be used for other absorber medium before detector crystal (absorption in the air, and in crystal coating), μ_c and d_c are the same values for the detector crystal.

$$d_{eff}(E_0, E) = \frac{1}{\mu(E_0)/\sin\theta_0 + \mu(E)/\sin\theta_1} \cdot \left[1 - \exp\left(-\left(\frac{\mu(E_0)}{\sin\theta_0} - \frac{\mu(E)}{\sin\theta_1}\right)d\right)\right] \tag{1.7}$$

$\mu(E_0)$ and $\mu(E)$ - lineal absorption coefficients in sample matrix for exciting and fluorescence radiation, θ_0 and θ_1 - are the incidence angle of the excited radiation and exit angle for fluorescence from the sample surface, d is the sample thickness. Effective thickness of fluorescence exit can be expressed in the more elegant way, like this

$$d_{eff} = d_{\infty/2} \cdot \left[1 - \exp\left(-\frac{d}{d_{\infty/2}}\right)\right]$$

$$d_{\infty/2} = \frac{1}{\mu(E_0)/\sin\theta_0 + \mu\left(E_l^e\right)/\sin\theta_1} \tag{1.8}$$

Here $d_{\infty/2}$ is effective fluorescence exit thickness for semi-infinite sample.

The lineal absorption coefficients for sample matrix can be expressed by standard way by weighted sum over the all matrix components:

$$\mu(\text{E}) = \rho \sum_m C_m \cdot \sigma_m^{abs}(E) \tag{1.9}$$

Here ρ - the sample density, C_m - concentration of the m-th component of the matrix, and $\sigma_m^{abs}(E)$ is absorption cross-section of the m-th matrix component for photon with energy E.

The spectrum background can be described by the polynomial or exponential polynomial with number of the parameters B_k which also can be fitted during fitting procedure. Oftene the some spectrum

preprocessing, like peaks removing or interpolation of the spectrum basis gives a simple ways for background accounting.

Thus, the total vector of the parameters should include the calibration parameters (E_b, g, No, gap), background parameters (B_k) and the series contribution coefficients (C_e). The last values are the final goal of the spectrum processing and result value can be finally used for quantitative analysis.

The fitting procedure is search of the parameter set which minimize difference from the simulated spectrum (in according with (1.1)) and real measured spectrum. As a rule this minimization is performed by least square algorithms.

For calculation of all above mentioned function a special tables of correct X-ray data is necessary to obtain the values of next parameters: $E_l^e, T_l^e, \sigma_m^{abs}$.

In current realization, the X-ray data used in the calculation are taken from X-ray library [2]. This library has a big number of the binding for different programing languages. In current work the Python interface was used.

For least square minimization the curve_fit function from Python scipy module was used. [3]. Functin has a variety of the operational option and work very reliable and robust.

Some preliminary calculation are implemented with using the Python numpy module, which combine the comfortable application for numeric calculations and fast arrays function.

Now the code for XRF spectra processing can be used in the Python script for treatment the set of spectra. Graphic user interface for simplifying common operation of the spectra processing is under development.

Results

Some results for using developed code for processing are presented on the Figure 1 and Figure 2.

Figure 1 shows the results of the processing of the geological sample (BIL-1, Russian standard for Baikal lake bottom sediments). This sample has a big variety element concentrations and many peaks overlapping cases. Lower plot on the Figure 1 shows the fitting residual which not excide 3σ level for the individual spectrum channels.
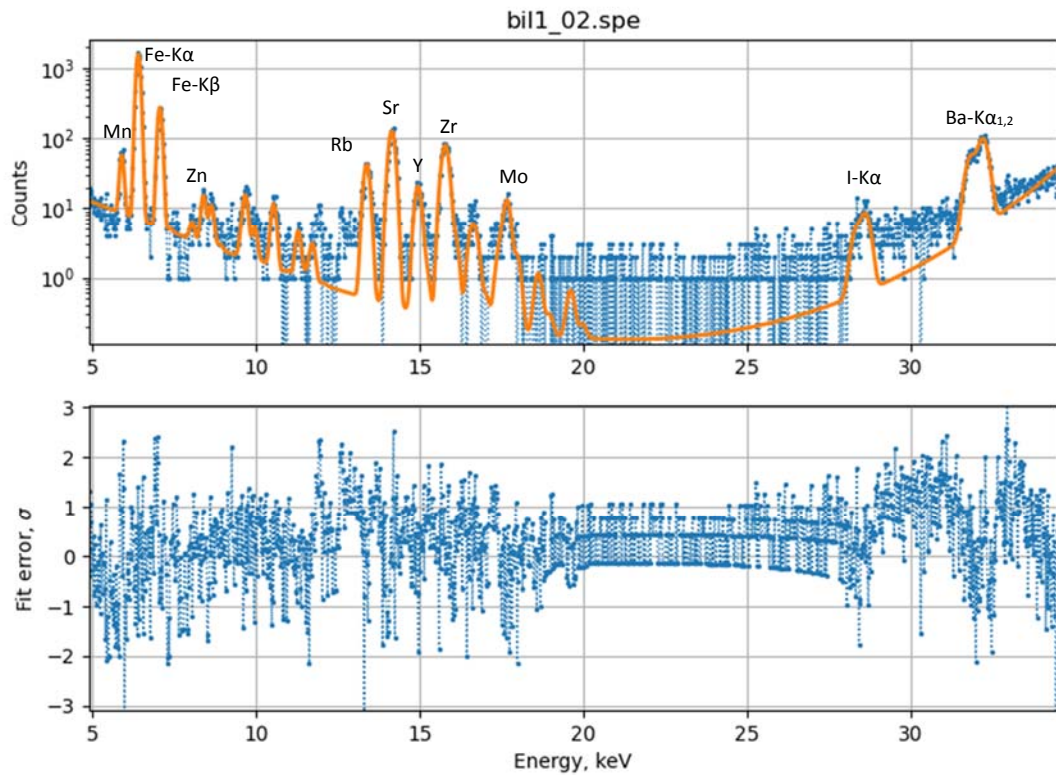
Figure 1. The results of the processing of the geological sample (BIL-1, Russian standard for Baikal lake bottom sediments). Lower plot shows the fitting residual.

Figure 2 presents the results of the spectrum processing for sample with heavy matrix (Lu) with some additions of the lighter elements.
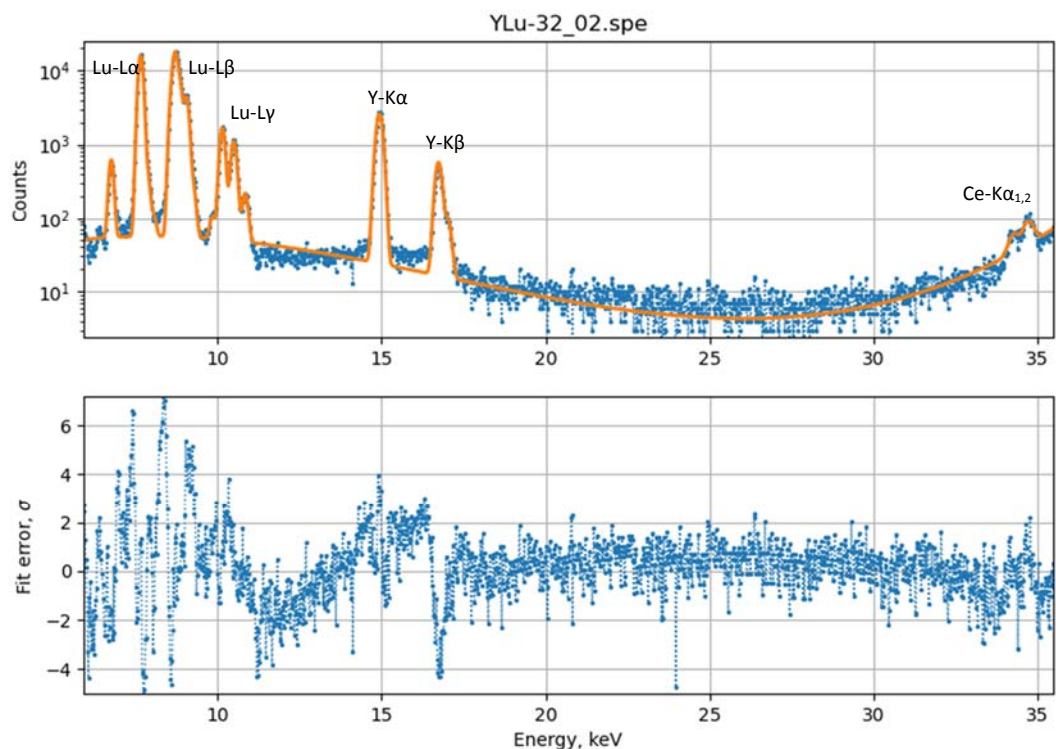
Figure 2 Results of the spectrum processing for sample with heavy matrix (Lu).

Because of the relative intensities for elements X-ray series strongly depend from matrix absorption, this result demonstrates a good quality of the matrix absorption accounting.

Code was tested in the new beamline for hard SR-XRF analysis on the VEPP-4M storage ring (Budker Institute of Nuclear Physics, Novosibirsk, Russia). Beamline creation was supported by RFBR grant 17-29-05016 офи_м.

Conclusions

The modern free software libraries make possible to creation simple and reliable code for X-ray fluorescence spectrum processing. This approach was tested for XFR analysis of different sample on the SR-XRF beamline in the Budker Institute of Nuclear Physics (Novosibirsk, Russia).

References

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