X-ray fluorescence analysis of low concentrations metals in geological samples and technological products

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Abstract. For the past several years many nuclear physics methods of quantitative elemental analysis have been designed. Many of these methods have applied in different devices which have become useful and effective instrument in many industrial laboratories. Methods of a matter structure analysis are based on the intensity detection of the X-ray radiation from the nuclei of elements which are excited by external X-ray source. The production of characteristic X-rays involves transitions of the orbital electrons of atoms in the target material between allowed orbits, or energy states, associated with ionization of the inner atomic shells. One of these methods is X-ray fluorescence analysis, which is widespread in metallurgical and processing industries and is used to identify and measure the concentration of the elements in ores and minerals on a conveyor belt. Samples of copper ore with known concentrations of elements, were taken from the Ural deposit. To excite the characteristic X-rays radionuclide sources $^{109}$Cd, with half-life 461.4 days were used. After finding the calibration coefficients, control measurements of samples and averaging of overall samples were made. The measurement error did not exceed 3%.

1. Introduction
Quantitative X-ray fluorescence (XRF) analysis involves the conversion of measured fluorescent intensities to the concentration of the analytes [1]. XRF raw data is the number of counts of element-specific fluorescent X-ray energies received in an XRF instrument detector. This raw data is visualized in a spectrum graph, where the x-axis represents element-specific fluorescent energies, and the y-axis represents counts or pulses. In a first approximation, the concentration for analyte in the samples is equal:

$$C_i = K I_i,$$

where $C_i$ is the concentration of the analyte, $I_i$ – intensity which have been measured for each analyte element, $K$ – calibration coefficient.

In this work the results of Wavelength Dispersive X-ray Fluorescence (WDXRF) were used for further calibration. WDXRF analysis is more accurate then XRF, but there is no possibility to use the WDXRF analysis in the manufacturing conditions for rapid analysis on the conveyor. Because this technique implies the homogeneity of the samples which is achieved with careful sample preparation. Also, methodology for conducting this analysis requires a great deal of precision in the construction of
the experimental geometry. XRF analysis can give experimental information faster and doesn't require careful preparation of samples. Therefore, it is preferable on the mining factories.

The average value, which is given at the end of the paper, was considered for the following reason – enrichment processes includes adding reactants in quantity grams per ton, depending on the concentration of copper in the large volume of ore. That’s why, adding of the reactants is required availability of the correct average value of the copper concentration in the active volume.

2. Implementation
Copper samples taken from the Ural deposits were chosen to perform the experiment. These samples were marked from 1 to 17 milled to a powder and sent to the Moscow Institute of Experimental Mineralogy for defining the concentrations of elements in this samples use WDXRF analysis. The results of this analysis are shown in table 1, measurement error did not exceed 5%.

| sample | mass fraction of copper, % | sample | mass fraction of copper, % | sample | mass fraction of copper, % |
|--------|---------------------------|--------|---------------------------|--------|---------------------------|
| 1      | 0.66                      | 8      | 0.84                      | 15     | 0.88                      |
| 2      | 0.8                       | 9      | 0.6                       | 16     | 1.35                      |
| 3      | 0.71                      | 10     | 1.1                       | 17     | 1.46                      |
| 4      | 1.05                      | 11     | 1.5                       |        |                           |
| 5      | 0.52                      | 12     | 1.6                       |        |                           |
| 6      | 0.47                      | 13     | 3.13                      |        |                           |
| 7      | 0.7                       | 14     | 2.15                      |        |                           |

For sample excitation four sources $^{109}$Cd, with an activity equal 40 mCi were used. Radionuclide $^{109}$Cd distributed within the ceramic matrix which is placed into the insert of tungsten alloy. Typical dimensions of the source are D=8 mm, H=5 mm, d=5 mm, h=1.2 mm. Structure of the $^{109}$Cd source is shown on figure 1.

![Figure 1. Structure of $^{109}$Cd source.](image)

The half-life of sources is 461.4 ±1.2 days. Photon energy range is:

- Ag X$K_{\alpha2}$ 22keV
- Ag X$K_{\alpha1}$ 22.2keV
- Ag X$K_{\beta2}$ 25keV
- Ag X$K_{\beta1}$ 25keV

Amptek Si-Pin detector with resolution 210 eV for Cu K$\alpha$ was used for detection of characteristics X-rays. The count rate of characteristic lines for all the samples were measured for 3 minutes. Error of measuring of the spectral line intensity for Cu K$\alpha$ did not exceed 4%. Some resulting spectrum is
shown below (see figure 2). Values of measured intensities for Cu Kα line for all 17 samples are shown in table 2. The intensities are normalized by a factor 42.7.

![Spectrum of the sample 13 (Cu\textsubscript{20} (% = 3.13)].

Based on the data from tables 1 and 2 the calibration curve has been constructed (see figure 3).

| sample | \(I_i\) (counts per sec) | \(I_i\) (counts per sec) | \(I_i\) (counts per sec) |
|--------|--------------------------|--------------------------|--------------------------|
| 1      | 2.7                      | 8                        | 3.2                      |
| 2      | 3.5                      | 9                        | 2.4                      |
| 3      | 3.0                      | 10                       | 3.9                      |
| 4      | 4.2                      | 11                       | 6.2                      |
| 5      | 2.2                      | 12                       | 6.6                      |
| 6      | 1.9                      | 13                       | 12.5                     |
| 7      | 2.8                      | 14                       | 8.8                      |

**Figure 2.** Spectrum of the sample 13 (Cu\textsubscript{20} (% = 3.13)).

**Table 2.** Measured Cu Kα intensities (Error did not exceed 4%).
Figure 3. Calibration curve. The dependence of measured copper intensities on the mass fractions of copper in the samples (see table 1 and 2). Experimental errors are within the data points.

Dependence is described by the equation (1), approximation error is equal 3%.

\[ I_{Cu} = 4.08C_{Cu} - 0.07. \] (1)

Hereafter control measurements of samples intensities have been made. After that, the values of the mass fractions of copper for all samples were calculated using equation (1), error didn’t exceed 11%. The average values for the mass fraction of copper have been calculated using following formula:

\[ C_{mean} = \frac{\sum_{N=1}^{N} C_N}{N}. \]

Average value of the mass fractions of copper for WDXRF analysis is equal: \( C_{meanWDXRF}(\%) = 1.15\pm0.07. \) Whereas, average value of the mass fractions of copper for XRF analysis is equal: \( C_{meanXRF}(\%) = 1.13\pm0.03. \) Errors here were defined not as error of an average for several measurements but as error of indirect measurements to demonstrate applicability of the method described in article.

3. Conclusion
The dependence of the measured copper intensities on the copper mass fractions was obtained and it will be used in manufacturing processes for determining the concentration of copper in the ore coming from the mine to the conveyor belt.

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References
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