Algorithm for applying regression analysis to determine the concentration of the main component in mineral raw materials by X-ray fluorescence method

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Abstract. X-ray fluorescence analysis (XRF) is currently in high demand in such branches of science and technology as metallurgy and geology. Today, it is important to create such methods of X-ray fluorescence analysis that would provide high accuracy of the results obtained along with a short execution time. The basic work is a technique, the essence of which is the use of regression analysis to determine the content of gold, as the main component in jewelry alloys. The technique uses a training sample that contains correlated radiation intensities of sample components with their gold content, determined by the assay method of analysis. In this paper, it is proposed to apply a similar approach to the analysis of mineral raw materials. Raw materials from the same deposit may have a similar composition, which allows you to collect enough statistical data to apply regression analysis. The paper proposes an enlarged algorithm for the development of such methods of X-ray fluorescence analysis. Such methods are of limited use, since they depend on the representativeness of the training sample and therefore can only be used to analyze materials of the same type, but their strengths are high accuracy and low time costs.

1 Introduction

Today, X-ray fluorescence analysis (XRF) is widely used in various areas of human life, from medicine [1] and biology [2, 3] to metallurgy [4] and geology [5-7]. X-ray fluorescence analysis has become widespread due to the high speed of execution and the relatively high accuracy of the results (under a number of conditions).

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As is known, the essence of XRF is to irradiate the sample with X-ray radiation, due to which the sample begins to fluoresce, i.e., emit waves of different spectra. The ranges of the emitted spectra depend on the composition of the test sample.

X-ray fluorescence analysis can be qualitative, semi-quantitative and quantitative [8].

In the course of qualitative XRF, only the composition of the sample is determined, without specifying the proportions of each of the determined components in the total composition.

In the course of semi-quantitative analysis, the approximate content of the components included in the sample is determined by correlating the radiation intensity of various spectra with a limited number of values of standard samples embedded in the software and hardware of the analyzer (spectrometer). These values of standard samples are sets of radiation intensities that correspond to the content (often in percent) of the analyzed components in the sample. Such an analysis is not highly accurate, since the set of values of standard samples embedded in the spectrometer is limited, and the characteristics of the cathode ray tube often begin to change with time, so the intensity of the radiation spectra of the same sample at different times may differ by some amount.

In the course of quantitative X-ray fluorescence analysis, the instrument is calibrated before starting work. It can be carried out once a day, once per shift, before taking each new batch of samples, before starting to take samples of a certain nomenclature, or before taking each sample. During calibration, standard samples are taken with a predetermined content of the components to be determined. In the course of subsequent measurements, the shift of the lines of their spectra is taken into account when determining the analyzed components in the test sample. This type of analysis is the most accurate in comparison with other types of XRF, but the time of its implementation exceeds the time of qualitative and semi-quantitative X-ray fluorescence analysis.

Thus, we can conclude that the task of performing XRF with high accuracy in a short time is relevant. One possible solution could be to combine the advantages of quantitative and semi-quantitative analysis.

2 Materials and methods

X-ray fluorescence analyzers (XRF spectrometers) are devices for determining the concentration of chemical elements in monolithic and multilayer samples using the X-ray fluorescence method.

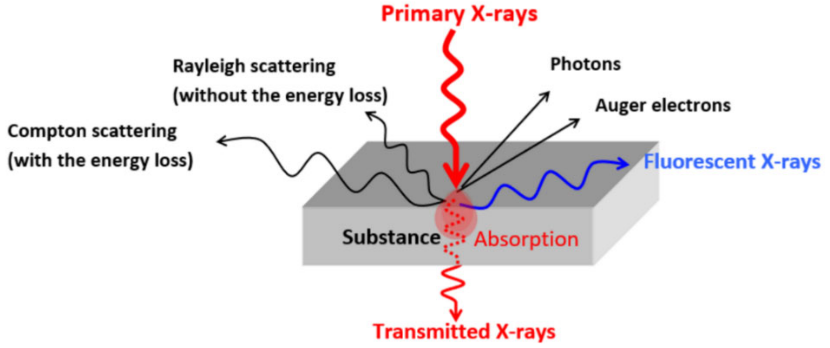

Fig. 1. Interaction of X-rays with a substance (source: https://www.horiba.com/gbr/scientific/).

X-ray fluorescence spectrometry is an analysis method used to determine the concentrations of elements from Beryllium (No. 4) to Uranium (No. 92) in the range from fractions of ppm to 100% in substances and materials of various origins. X-ray fluorescence analysis is widely used both in industry and in science due to its versatility, accuracy and speed of measurements, as well as ease of operation.

A method is used based on the principle of measuring the spectrum of secondary X-ray radiation [9]. An illustration of the method is shown in Figure 1.

The primary x-rays generated by the x-ray tube irradiate the analyzed sample and cause secondary x-rays, the spectrum of which depends on the elemental composition of the sample. An X-ray tube is used as a source of excitation. The calculation of the mass fraction of the analyzed elements is based on the dependence of the radiation intensity on its mass fraction in the sample. In the calculation, a standard-free version of the method of fundamental parameters is used.

The test sample is irradiated with an x-ray tube. As a result of the interaction of X-ray radiation with the substance in the used sample, secondary fluorescent radiation arises, in the spectrum of which there are characteristic lines of those elements that are part of the sample. The presence of lines of this element in the spectrum indicates its presence in the sample, and the intensity of these lines makes it possible to judge the concentration of elements.

3 Results

In [10], the authors describe the application of the technique of X-ray fluorescence analysis of gold in jewelry alloys, which just combines the advantages of quantitative and semi-quantitative analysis. It is based on a linear regression that establishes a relationship between the gold content in the sample and the radiation intensities of the elements included in the analyzed alloy. The regression equation chosen by the methods of the influencing factor and estimation of the correlation of residuals with the influencing factor takes into account the effect of such elements as Ag, Cu, Zn, Ni, and Pd on the intensity of the gold line.

To find the coefficients of linear regression, a system of linear algebraic equations is solved, for the compilation of which virtual calibration samples (VCS) are used - the results of the analysis of real samples (intensity of X-ray lines of elements and values of the gold content obtained by assay analysis), placed in an electronic database (DB). VCS, for which the line intensities of the elements are close to those measured for the analyzed sample, are selected from the database using a filter: for each of the elements (metals) in the sample, its filter value is determined [10].

As the authors of the work summarize, the application of the developed technique made it possible to significantly reduce the analysis time, while the error in the results of gold determination does not exceed 0.13%, which is comparable with the assay method [10].

The technique described above turned out to be workable, since the chemical composition of jewelry alloys is regulated by GOST 30649-99 «Precious metal-based alloys. Marks», i.e., the content of their constituents is regulated. Similarly, one can argue in the analysis of not only secondary (for example, jewelry scrap), but also mineral raw materials. If mining is carried out at one deposit, then the mineral composition of the raw material should be approximately the same or change smoothly as the deposit is developed. This circumstance allows us to conclude that dependencies can be found between the contents of the components of such raw materials, i.e., regression analysis can be applied to determine the principal component, as in the methodology described above.

Thus, an algorithm can be drawn up for the development of such methods, consisting of the following steps.

Step 1. To determine the main component, the content of which in the sample is the most critical (in the example above, this component was gold).

Step 2. To determine the composition of the analyzed raw materials by conducting a series of tests with high-precision analysis methods.

Step 3. To collect a sufficient amount of statistical data, which will include the intensities of the radiations of the sample obtained on the X-ray spectrometer, correlated with the exact content of the main component in each such sample. The size of the statistical sample must be sufficient to be considered representative. The personal recommendation of the author of the work is at least 2000 measurements.

Step 4. To choose the most appropriate form of regression for solving the problem and evaluate its applicability, as was done, for example, in [11].

Step 5. To conduct laboratory tests on real samples, the number of which is not less than the size of the training sample.

Step 6. To make adjustments if necessary and return to step 5. If there are no adjustments, go to step 7.

Step 7. To register the method (if necessary).

Step 8. To start the process of introducing the methodology into commercial operation.

4 Discussion

The algorithm described above may be useful only for the analysis of materials that have a relatively similar composition. In case of non-compliance with this condition, an analysis of this kind will either be impossible, or it will be necessary to accumulate a sufficient amount of statistics to conduct a regression analysis.

This circumstance limits the applicability of this approach. However, in those areas where it is applicable, its effectiveness (high accuracy at high speed) can be significant.

5 Conclusion

The article considers one of the options for using X-ray fluorescence analysis in conjunction with the use of regression. In addition, an algorithm for the formation of this kind of analysis methods is given. This algorithm can be useful for those specialists who are engaged in X-ray spectral analysis of materials whose composition does not change over time or changes smoothly (so that new statistics can be accumulated in time).

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