Quantitative x-ray spectral determination of rare-earth metals in products of metallurgy

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Abstract. A technique for x-ray spectral quantitative determination of lanthanides in solid products of metallurgical industries have been developed and coupling equations have been derived that make it possible to calculate the concentration of rare earth metals with an accuracy that meets the requirements of the technological process. The study performed samples of the analyte with monochromatic gamma or x-ray radiation with simultaneous recording of the intensities of the characteristic radiation and incoherently scattered radiation by the same breakdown of the primary radiation, the concentration measurement of the element being determined is carried out according to the analytical parameter taking into account the effect of the background of the characteristic radiation. The technical result was the provision of the possibility of determining the concentration of elements in samples of different chemical and material composition, having a different structure and density, without identifying the phase composition, but with a preliminary correction of the background.

1. Introduction

Wet-process phosphoric acid is obtained from apatite concentrate by the sulfuric acid dihydrate decomposition scheme. The need for operational control of the crystallization extraction of rare earth metals from this solution, the researcher is faced with the task of finding a high-Express method of quantitative determination of lanthanides crystallized in the form of phosphates or fluorides on a solid matrix, with reproducibility and accuracy, satisfying the requirements of the process.

Modern instrumental methods are considered by researchers of the Moscow University of Russia [1], Kurchatov Institute [2] and researchers of the National University of Cordoba [3]. The analytical characteristics and the figures of merit of various analysis techniques are compared, among which atomic emission spectrometry, inductively coupled plasma mass spectrometry (ICP-MS), and neutron activation analysis (NAA) occupy a special place.

Despite the fact that a share of x-ray fluorescence analysis (XRF) is not large, it should be mentioned. This method constitutes 1.5% of the foreign research and occupies a rather large niche in domestic publications, 11% [1]. Undoubtedly, this is associated with a high level of development of XRF in our country.

The advantages of using x-ray spectrometry, firstly, is the relative simplicity of the sample preparation process which does not require the transfer of the analyzed product to the liquid phase. Secondly, it is the ability to analyze liquid and solid samples in almost any objects, including complex natural mixtures.
The disadvantages of this method are connected with the nonlinear characteristics of the detector of x-ray spectrometers and the dependence of the background scattering spectrum on the elemental composition of the matrix. For example, in [4,5], for the determination of basic and impurity components including REM in eruptive rocks. The calibration samples were prepared from high purity reagents, rather than from standard rock samples. The detection limits were from 0.5 to 0.7 mg/kg for Ce and Gd, respectively.

In [6], the content of the REMs in apatites was determined by wavelength-dispersive XRF analysis. The determination was performed using one reference lanthanum sample and the intensities for the REMs were calculated by the fundamental parameter method using the theoretical line superposition correction.

In [7], the determination of the REMs in rocks by the XRF and the ICP-MS methods is described. The correctness of the obtained results has been evaluated and possible reasons for systematic error have been established.

XRF analysis was used to determine high contents of \( \text{Y}_2\text{O}_3 \) (45–75 wt %) in rare earth concentrates [8]. To reduce the impact of the composition of the sample on the intensity of the analytical \( K\alpha \) line of yttrium, the samples of concentrates were diluted with \( \text{Ta}_2\text{O}_5 \) powder.

In [9], the application of electron microprobe x-ray spectrum analysis to determine high contents (0.5–30 wt %) of La, Pr, and Nd in their minerals is described.

A significant increase in the expression and accuracy of the determination, both by eliminating the matrix effect and by eliminating the dynamic errors is achieved by the introduction as a normalization factor of the intensity of the x-ray tube anode radiation incoherently scattered by the sample.

Concerning this fact, the authors developed the method of x-ray fluorescence analysis using the x-ray spectrometer "SPECTROSCAN G" (Ag – anode, the voltage on the X-ray tube-40 kV, the current in the anode circuit-100 μA, the thickness of the beryllium window-10 μm, the angle of entry and incidence of radiation on the sample 90°). The measurements were carried out according to the scheme of wave dispersion with LiF200 crystal analyzer, which allows one to register radiation in the first and second order of reflection. x-ray terms of the L-series of the characteristic radiation of the element were selected to determine the REM.

The essence of the method is to determine the concentration of the desired element \( C_i \) on the conclusion of equations relating to the ratio of the intensity of the analytical line of the characteristic radiation of the element to the intensity of incoherent scattered radiation of the anode tube:

\[
C_i = F(I_i/I_{Ag\, no}, I_2...I_n). \quad (1)
\]

In [10,11], the possibility of using the ratio \( I_i/I_{Ag\, no} \) as an analytical parameter in connection with a slight dependence on the sample matrix was theoretically substantiated.

2. Materials and methods
The object of the research was multicomponent industrial phosphoric acid solutions containing 0.1% REM, concentrates of phosphates or fluorides of REM, obtained by crystallization from solutions of phosphate acids supersaturated with lanthanides.

With the aim of deriving the coupling equations to calculate the concentrations of Ce and the possibility of quantitative determination of other rare earth elements La, Eu, Sm, Er in the solid products and solutions in the production of wet-process phosphoric acids created by the array of calibration samples by diluting the starting material for crystallization of the matrix material have a minimum impact on the intensity of the lines of L-series of cerium.

The set of samples is prepared by mixing \( n \) parts of the crushed materials of the solid matrix with \( m \) parts of boric acid in the vibration mixer. The mixing time is not less than 5 min. From the obtained mixtures with a hydraulic press, pressure 20 t/cm² compressed tablets of thickness 2 – 3 mm and a diameter of 1.5 cm as an example, table 1 shows a set of calibration samples according to cerium.
Table 1. Dilution and percentage of calibration samples.

| Weight CePO₄, g | Filler weight (boric acid), g | Concentration Ce, % |
|-----------------|-----------------------------|--------------------|
| 10              | 0                           | 59.60              |
| 4.5087          | 0.504                       | 53.58              |
| 4.0095          | 1.1341                      | 46.44              |
| 3.5004          | 1.5205                      | 41.53              |
| 3.0018          | 2.0149                      | 35.65              |
| 2.4979          | 2.5041                      | 29.75              |
| 9.0063          | 0.9888                      | 2.94               |
| 2.5067          | 2.5021                      | 1.47               |
| 2.5136          | 2.4837                      | 0.73               |
| 2.6208          | 2.5343                      | 0.36               |
| 2.8489          | 2.5897                      | 0.17               |
| 2.5134          | 2.5507                      | 0.08               |
| 2.1049          | 2.1127                      | 0.04               |

Analogically to cerium, sets of calibration samples for erbium, samarium, europium, and lanthanum were prepared in the concentration range from 0.05 to 4%.

3. Results and discussion

The authors obtained the linear relationship of analyte concentration from ratio of the intensity of the line La - Ce to Inc decoherence the intensity of the scattered radiation Ag, which allows one to obtain a linear equation of the relationship. The coupling equations for the following ranges of Ce concentrations are derived by the method of multiple regression from 30 to 60% and from 0.04 to 3%, taking into account these analytical lines (see Figures 1 and 2).

Figure 1. The calibration dependence on cerium in the concentration range of 30-60%.
Figure 2. The calibration dependence on cerium in the concentration range 0.04-3%.

The coupling equations derived by the least square method for the concentration range from 0.04 to 3% for cerium are as follows:

\[
C(Ce) = 0.7874 \frac{I_{La}}{I_{Agnc}} - 3.6997. 
\] (2)

Accordingly, for the range of 30-60%:

\[
C(Ce) = 1.8266 \frac{I_{La}}{I_{Agnc}} - 0.1049. 
\] (3)

Coupling equations for erbium, samarium, europium and lanthanum in the range from 4 to 0.05%:

\[
C(Er) = 0.0729 \frac{I_{La}}{I_{Agnc}} - 0.089, \] (4)

\[
C(Sm) = 3.257 \frac{I_{La}}{I_{Agnc}} + 0.0134, 
\] (5)

\[
C(Eu) = 0.2304 \frac{I_{La}}{I_{Agnc}} - 0.1124, 
\] (6)

\[
C(La) = 2.657 \frac{I_{La}}{I_{Agnc}} - 0.3015, 
\] (7)

where \( I_{La}, I_{Agnc} \) - intensity (count rate of the detector) of the analytical lines Ce of the characteristic radiation of the sample, \( C(i) \) is the concentration of REM in the mass. %.

The results of measurements of the sample model and technological products according to the obtained coupling equations are presented in tables 2 and 3:
Table 2. Calculated concentrations of model solutions.

| Cerium | Erbium |
|--------|--------|
| C, %   | C₀, %  | Rel. er. of the array, % | C, %   | C₀, %  | Rel. er. of the array, % |
| 1.95   | 0.71   | 1.85                   | 1.96   | 0.39   | 1.81                   |
| 1.93   | 1.96   | 1.69                   | 1.93   | 1.61   | 1.7                    |
| 2.02   | 1.96   | 3.09                   | 1.85   | 1.96   | 4.78                   |
| 1.99   | 1.31   | 1.81                   | 2.03   | 1.69   | 3.71                   |
| 0.29   | 8.05   | 0.27                   | 0.31   | 2.69   | 6.31                   |
| 0.31   | 3.85   | 0.26                   | 0.32   | 5.1    | 11.53                  |
| 0.3    | 5.81   | 0.27                   |        |        | 8.9                    |

Table 3. Calculated concentrations of technological products.

| Wet-process phosphoric acid | Cerium concentrate |
|-----------------------------|--------------------|
| C, %                        | C₀, %  | Rel. er., % | Rel. er. of the array, % | C, %   | C₀, %  | Rel. er. | Rel. er. of the array, % |
| 0.108                       | 7.7    | 1.01        | 58.01                   | 0.103  | 2.9    | 1.28     | 57.85                   |
| 0.111                       | 11.2   | 0.22        | 58.73                   | 0.097  | 2.7    | 1.66     | 57.63                   |
| 0.098                       | 0.1    | 1.57        | 58.01                   | 0.098  | 2.4    | 6.7      | 58.6                    |
| 0.112                       | 12     | 3.53        | 56.53                   | 0.112  | 6.5    | 1.43     | 57.76                   |
| 0.108                       | 8.4    | 1.55        | 57.69                   | 0.108  | 8.4    | 2.44     | 57.17                   |

4. Conclusion
As a result of the research, the method of x-ray spectral quantitative determination of lanthanides in the products of metallurgical industries was developed. The equations of communication allowing one to calculate the concentration of REM in multicomponent systems of a different matrix with the accuracy satisfying the requirements of the technological process are derived. The method of preparation of calibration samples in the range of cerium concentrations from 0.04 to 60% with filler and other REM (Eu, Er, La, Sm) in the range from 4 to 0.05% was worked out.

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