Technical Note

Determination of rare earth elements in combustion ashes from selected Polish coal mines by wavelength dispersive X-ray fluorescence spectrometry

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Adam Smoliński [a,*], Marek Stempin [b], Natalia Howaniec [a]

[a] Department of Energy Saving and Air Protection, Central Mining Institute, Plac Gwarków 1, 40-166 Katowice, Poland
[b] Department of Environmental Monitoring, Central Mining Institute, Plac Gwarków 1, 40-166 Katowice, Poland

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ABSTRACT

The aim of the experimental works presented in this paper was to develop a method using wavelength dispersive X-ray fluorescence spectrometry (WDXRF) in order to determine the content of 16 rare earth elements (REEs) and the concentration of the said elements in 169 samples of combustion ash of coals coming from ten Polish coal mines, as well as to validate the method. It was found out that there is a clear diversity in the levels and ranges of the variability of REEs occurrence in coal ashes. The average content of cerium, lanthanum, and scandium amounts to 198.8 $\mu g \cdot g^{-1}$, 76.5 $\mu g \cdot g^{-1}$, and 52.4 $\mu g \cdot g^{-1}$ respectively, whereas for such metals as europium, holmium, lutetium, terbium, and thulium, the average content does not exceed the level of 5 $\mu g \cdot g^{-1}$ (the average content for these metals amounts to 1.2 $\mu g \cdot g^{-1}$, 1.4 $\mu g \cdot g^{-1}$, 0.3 $\mu g \cdot g^{-1}$, 1.3 $\mu g \cdot g^{-1}$, and 0.6 $\mu g \cdot g^{-1}$, respectively). In addition, this paper presents an analysis of data obtained by means of hierarchical clustering analysis. Simultaneous interpretation of the dendrogram of objects (coal ash samples) and the color map of the experimental data allowed a more in-depth analysis of the relationships between the clustered coal ash samples from different coal mines and the content of the rare earth elements.

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1. Introduction

Inductively coupled plasma–optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence (XRF), and neutron activation analysis (NAA) constitute the most commonly applied techniques for the determination of rare earth elements (REEs) [1–6]. The ICP-OES technique is mostly applied to analyze liquid or solid samples after they have been mineralized in oxidizing acids. It cannot be used, though, to detecting REEs in solid samples. One of the advantages of ICP-OES technique is that it can be used to simultaneous determination of a wide range of elements within a large scope of their concentrations. More often than not, however, the levels of REEs occurrence in the analyzed samples are below the limits of detection. In addition, organic compounds and inorganic salts, being the main components of the samples, cause matrix effects. A recently developed ICP-MS technique has become one of the most important tools to determine the content of REEs [3,7]. The major advantages of this technique are its high precision and accuracy, large linear scope, possibility of simultaneous analysis of numerous elements, and possibility of isotopic measurements. Unfortunately, numerous spectral interferences pose an analytical problem in its application. In order to limit the

spectral interferences and matrix effects, a preliminary separation of REEs from matrix elements is used. However, the separation methods are very complicated, time-consuming, and can always be a potential source of random, or even systematic errors.

The NAA technique has been increasingly applied in direct analysis of REEs content in solid samples; yet it has an obvious disadvantage because of the occurrence of numerous interferences from the main elements and because of long radiation time [2,8–11]. On the other hand, it is characterized by high sensitivity and, hence, the resulting low detection limits. The XRF technique offers the possibility of determining REEs in solid materials while it does not require complex preparation stage of the analyzed sample; it also allows for simultaneous determination of both trace and main components [5,6,12–15].

However, there are a few serious problems that have to be solved before WDXRF technique can be successfully applied for the determination of REEs in solid materials, including hard coal ashes. The most important of them are matrix effects (absorption and enhancement) and overlapping of peaks. Ideally, the intensity of an analytical line is linearly proportional to the concentration of the analyte. However, the intensity of an analytical line does not depend solely on the concentration of the respective element; it also depends on the presence and concentrations of other elements. These other elements may lead to absorption or to enhancement of X-rays. Both these effects occur in coal ash analyses because of its diversified chemical composition. Therefore, they

cannot be neglected and the best way to minimize the matrix effects in case of REEs determination is the application of the background correction method. At present, the WDXRF spectrometers available on the market are all equipped with the software, which using mathematical algorithms developed specifically for this purpose, can deal with this problem quite efficiently. Overlapping peaks are more problematic in the determination of rare earth elements in solid samples containing even trace amounts of heavy metals belonging to the IV period. Lα lines are REEs analytical lines (except for scandium and yttrium). The lines occur within angle 2θ range from 82.88° for lanthanum to 47.41° for lutetium. In the same angle 2θ range, there also occur spectral lines Kα and Kβ of IV period elements, from titanium to zinc, respectively (Kα Ti, 86.11°; Kα Zn, 41.78°). These lines are of high intensity not only because, as being K series spectral lines, they are better induced at given X-ray tube current conditions but also because the contents of titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, and zinc 1000-fold or even 10,000-fold exceed the contents of REEs in coal ashes. The LiF200 analyzing crystal used for diffracting the X-ray fluorescent spectrum of the induced sample cannot separate lines of similar wavelengths despite its high-resolution capacity. The ZSX Primus II spectrometer is equipped with top class detectors as well as analytics software, which enables peak deconvolution at the stage of developing calibration curves, and therefore it allows for determining all REEs.

Due to these analytical difficulties, it cannot be expected that limits of quantification in WDXRF method will be better or even equal to these, which can be obtained in ICP-OES, ICP-MS, and NAA techniques. However, WDXRF offers several advantages over other methods: sample preparation for X-ray measurements is neither expensive nor time-consuming and time of measurement is not long, usually of a few minutes. The simplicity of sample preparation means also that it is less likely to contaminate the sample or to lose the analyte in the process. Thus, although it may be difficult to determine concentrations of all REEs in solid materials with high accuracy and precision by WDXRF technique, it might be widely applied in evaluation of the level of concentrations of REEs in different solid materials in cost-effective and time-saving way.

In the existing literature, there are many papers concerning the determination of REEs in biological samples, waters, sediments, as well as geological formations such as rocks, minerals, ores, soils, grounds, and sands. However, the body of literature regarding the occurrence of REEs in hard coal is very limited [16]. Hanak's papers [17] emphasize the high content of cerium in Polish coals as compared with the average content of this element in coals worldwide. Parzentny [18], in turn, puts emphasis on the higher content of lanthanum in Polish coals as compared with coals worldwide. It is worth noting that all analyzed waste materials coming from coal combustion, demonstrate high contents of cerium (from 39 to 186 µg·g^{-1}) and lanthanum (from 16 to 86 µg·g^{-1}), which indicates the possibility of utilizing the waste materials as a future alternative source of the said elements. The precise identification of REEs occurrence in hard coal would address the urgent issue of the possible utilization of hard coal and coal waste materials, including the coal combustion or coal processing products, as a source of REEs.

The paper presents an original method of determining 16 REEs (except for promethium) in ashes coming from the combustion of Polish energy coals by means of wavelength dispersive X-ray fluorescence spectrometry (WDXRF) technique, the results of the method validation, as well as chemometric data analysis of 169 samples of ashes coming from the combustion of energy coals from 10 Polish coal mines.

2. Experimental

A method for the determination of REEs in the lowest possible range of concentrations by means of WDXRF was developed. On the basis of

this method, the level of occurrence of REEs in coal ashes coming from the combustion of Polish energy coals from various coal mines countrywide was estimated.

2.1. The method to determine REEs in coal ashes by means of WDXRF technique

Ten certified reference materials were applied for calibration. Eight of them were Chinese standard soils and stream sediments approved by China National Analysis Centre for Iron and Steel, Beijing, China, of code numbers NCS DC 73312, NCS DC 73321, NCS DC 73322, NCS DC 73324, NCS DC 73384, NCS DC 73385, NCS DC 73388, and NCS ZC 73312. The remaining two standards were limestone supplied by NIST–Standard Reference Materials, Gaithersburg, USA, and soil supplied by CANMET Mining and Mineral Sciences Laboratories, Ottawa, Canada. Two factors were taken into consideration in the selection of the standards. First, the standard should have possibly wide range of concentrations of REEs to give calibration curves fully covering the range of occurrence of earth elements in coal ash. Second, the standards should be varied in terms of the main chemical components (matrix). Standard coal ashes available on the market do not meet these requirements. It did not, however, affected the X-ray measurements since ashes from coal combustion in a muffle furnace at 815 °C were employed to prepare calibration samples. Concentrations of REEs in the standard ashes obtained were recalculated taking into account the loss on ignition in the combustion process.

2.1.1. The preparation of standard ashes and analyzed samples of coal combustion ashes for the WDXRF measurement

The samples of 3.0000 g ± 0.0002 g standard ash, 1.5000 g ± 0.0002 g cellulose, and 0.4500 g ± 0.0002 g graphite were first dried for 2 h at the temperature of 105 °C and then weighed on an analytical balance. The combined samples were then preliminary mixed in a weighing bottle for 1 min. The obtained mixture was quantatively transferred to a grinding mill and ground for 1 min at high speed of 1500 rpm. The ground sample was pressed in a hydraulic press (20 kN) to obtain a tablet durable enough to be subject to multiple X-ray measurements. For the preparation of all tablets for X-ray measurements (standards and analyzed samples), a HERZOG grinding mill HSM 100 A and a hydraulic press HTT40 were used. X-ray measurements were performed by means of a RIGAKU PRIMUS II sequential WDXRF spectrometer with Rh anode X-ray tube. The research was done with the application of fine collimator, analyzing crystal LiF200 and a scintillation counter as a detector. The time of the analytical line measurement was 60 s, whereas the time of background measurement was 30 s.

2.1.2. Optimization of apparatus measurement conditions and the selection of analytical parameters

Before the analytic application was created, peak profiles had been scanned in order to obtain data on the occurrence of spectral interferences and in order to determine the values of angle 2θ to measure the peak and the background. The values and the spectral interferences are presented in Table 1. In turn, Fig. 1 shows examples of X-ray spectra of the analytical lines neighborhood for chosen three REEs (cerium, dysprosium, and erbium).

In order to apply the method of peak deconvolution for coal ash samples, which are complex in terms of their matrix content, it is necessary to carefully align background measurement angle 2θ for each of the analyzed elements. The intensity of the background lines at the stage of the method calibration was used not only for the deconvolution of peaks but also for matrix effect correction.

There are two main quantitative analysis methods: the fundamental parameters method (FP) and the empirical calibration method (EP). The FP method is characterized by three restrictions. The first one is that all components present in a sample must be applied in quantification, so