Radioisotopic X-ray fluorescent analysis is widely used in elementary analysis, thanks to its relatively high sensitivity and the simplicity and indestructibility of the equipment required [1, 2]. This method has been used in determining the ash content and elementary composition of coal [2].

Coal is a multicomponent material, with a fuel (organic) component and a mineral (inorganic) component. The mineral component, which varies in elementary composition, contains compounds of aluminum, silicon, sodium, magnesium, sulfur, calcium, iron, and so on.

More than 95% of the mineral component consists of aluminum, silicon, calcium, and iron compounds. For most coal deposits, the elementary composition varies considerably, and there is no clear distribution pattern. That hinders the X-ray fluorescent analysis of coal.

In X-ray fluorescent analysis, it is important to correctly select the primary γ-ray energy for excitation of the X-ray fluorescence of the chosen element. The selection of the primary γ-ray source is usually based on the condition

$$3E_K > E_0 > 1E_K,$$

where $E_0$ is the energy of the primary γ radiation; $E_K$ is the energy of the element’s K absorption edge (the ionization potential).

As $E_0$ is shifted closer to the lower limit ($1E_K$), the excitation of X-ray fluorescence becomes more effective. As $E_0$ is shifted closer to the upper limit ($3E_K$), the method becomes more sensitive to the element of interest.

In practice, as a rule, the choice of the primary γ-ray source depends on the composition of the material being analyzed; the atomic number of the element of interest; the effective atomic number of the filler; and the variation in the composition. The goal is to find a balance between the sensitivity of the method and the effective excitation of fluorescence.

In selecting the equipment for X-ray fluorescent analysis, it is equally important to take care when choosing the parameters of the spectrometer with finite energy resolution.

The width of the spectrometer’s energy window must be correctly chosen because the window width $\Delta E$ in the X-ray fluorescent range of the element of interest (the analytic line) affects important parameters such as the relative sensitivity of the method and the statistical error in radioactivity measurements.

In X-ray fluorescent analysis, different approaches are adopted in selecting the optimal width of the spectrometer’s energy window close to the analytic line of the element of interest. This is of particular importance when using scintillation and gas-discharge proportional detectors with finite energy resolution.

The width of the spectrometer’s energy window is optimized so as to minimize the influence of equipment instability [1] and to obtain minimum threshold sensitivity [3]. From this perspective, the optimal parameters of the spectrometer depend primarily on the X-ray fluorescent energy of the element of interest.

Another option is optimization of the spectrometer’s parameters in the light of the contribution of the scattered γ radiation (background radiation) close to the analytic line of the element of interest [4]. The metrological characteristics of the analysis will vary as a function of the width of the energy window $\Delta E$ close to the analytic line of the element.

In particular, with decrease in $\Delta E$, the contribution of the background radiation declines. As a result, the method becomes more sensitive to the element of interest. However, the total intensity of the measured quanta also declines, with increase in the statistical error of the measurement.

With increase in $\Delta E$ on account of increase in the number of background γ quanta, the sensitivity to the element of interest decreases, and so does the relative statistical error of the measurement. There is an inverse relationship between the sensitivity to the element of interest and the most important metrological...
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parameter—that is, the precision in determining the concentration of the element. Hence, it is of critical importance to select the optimal width $\Delta E$ of the energy window for X-ray fluorescent analysis by a spectrometer with finite energy resolution.

In selecting the optimal width $\Delta E$ close to the analytic line $E_i$ of the element of interest, the goal is to minimize the measurement error (expressed in relation to the content of the element of interest)

$$
\Psi = \left( S \sqrt{N} \right)^{-1} = \min,
$$

where $S$ is the relative sensitivity (that is, the relative increment in the measured intensity with unit change in concentration of the element of interest); $N$ is the measured intensity close to the analytic line of the element of interest.

It is evident that $\Psi$ characterizes the error in determining the content of the element on account of statistical fluctuation in the measured intensity.

If we approximate the measured spectra of the secondary (scattered and fluorescent) radiation by a normal distribution and adopt the familiar principles of nuclear metrology, we may find the normalized optimal width of the energy window in the form

$$
\frac{\Delta E}{E_i} = \left[ \frac{R_R}{N} \left[ 1 + \frac{d}{\varepsilon - 1} \ln\left( \frac{2}{\xi} \left( \frac{R_F}{0.424} \right)^2 \right) - 1 \right] \right]^{-1}. \tag{2}
$$

Here $R = R_s/R_f$; $R_s$ is the energy resolution for the scattered radiation, and $R_f$ is the energy resolution for the fluorescent radiation. Likewise, $\varepsilon = E_s/E_i$; $E_s$ is the energy for the scattered radiation, and $E_i$ is the energy for the fluorescent radiation. Finally

$$
d = \frac{(R_R)^2 - 1}{2(\varepsilon - 1)},
$$

and $\xi = N_s/N_f$; $N_s$ is the intensity in the channel for the scattered radiation, and $N_f$ is the intensity in the channel for the fluorescent radiation.

In Fig. 1, we show the normalized error of the analysis as a function of the normalized width of the energy window, with different energy ratios of the scattered and fluorescent radiation. Regardless of the energy ratio $\varepsilon$, the correlation between the error and the normalized width of the energy window changes sign at some point.

It makes sense that larger $\varepsilon$ should be associated with a smaller contribution of background radiation and hence lower error. As the energy of the background radiation approaches the energy of the analytic line (as $\varepsilon$ declines), the region where the correlation is reversed is shifted to smaller $\Delta E$.

By means of the proposed model, we may assess how the intensities in the scattered- and fluorescent-radiation peaks affect the optimal width of the spectrometer’s energy window.

Since the loss of $\gamma$ energy on scattering is small in the low-energy region, the energy of the scattered $\gamma$ quanta is assumed equal to the energy of the primary radiation. We see in Fig. 2 that the optimal width of the spectrometer’s energy window declines with increase in intensity in the scattered-radiation peak (increase in $\xi$). That is the case at any energy of the primary $\gamma$ radiation. With increase in energy of the primary