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New Approach to the Determination of the Effective Wavelength of the Excitation Spectrum in Standardless X-ray Fluorescence Analysis of a Homogeneous Multicomponent Object

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Abstract—A simple algorithm has been developed for calculating the effective wavelength of the polychromatic emission spectrum of an X-ray tube upon excitation of X-ray fluorescence of a homogeneous object all components of which give rise to characteristic signals within the working wavelength range of a spectrometer used. The adequacy of this approach has been verified in the course of standardless X-ray fluorescence analysis of certified steel samples by the fundamental parameter method.

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The notion of effective wavelength of primary radiation is traditionally used for considering the polychromaticity of the emission spectrum of an X-ray tube in standardless (SL) X-ray fluorescence (XRF) analysis of multicomponent objects. The action of this component is equivalent to the excitation caused by all radiation of the continuous emission spectrum of the tube in the range from its short-wavelength limit to the absorption edge of the chemical element to be determined [1]. The use of the effective wavelength of an X-ray tube makes it possible to considerably reduce the volume of necessary calculations. The effective wavelength depends on the nature of an analyte, the elemental composition of a sample, the emission spectrum of an X-ray tube, and its filtration by the surface layers of the object. However, the effective wavelength is usually determined using complicated analytical expressions not quite suitable for performing numerical calculations [1–4]. In addition, in these expressions, virtual tube emission spectra are used in which the bremsstrahlung component is specified by a simple and, in general case, incorrect function (for example, by the Kramers function), while the relative intensity of characteristic lines is described by a universal function of the potential and anode material [2, 5]. The calculated spectrum is independent of the geometry of the X-ray tube, and this increases the error of the analysis results. The calculation of the effective wavelength requires knowledge of the elemental composition of the analyte, which is a priori unknown. In this context, some researchers have proposed to use simpler methods of calculation of this parameter [1, 5]. As a rule, the effective wavelength is empirically taken either as the midpoint of the range delimited by the short-wavelength edge of the tube emission spectrum and the absorption edge of the chemical element to be determined or as the average of theoretically possible values for this element. Inasmuch as the effective wavelengths thus selected depend only on the analyte nature and do not take into account the other above-mentioned factors and, hence, can differ noticeably from the true values, the correctness of the results of SL XRF analysis noticeably decreases [6]. The aim of the present work is to develop a new approach to calculating the effective wavelength of the emission spectrum of a given X-ray tube of a laboratory XRF spectrometer. The approach should be easy to formalize when developing numerical algorithms of SL XRF analysis of a multicomponent object all components of which give rise to characteristic signals within the working wavelength range of an XRF spectrometer.

ALGORITHM

The following expression is valid for the intensity of the XRF emission of element A with the wavelength λ_{fl} excited in the analyte at the depth d by the X-ray tube radiation with the wavelength λ_1 and the intensity I_1:

$$I_{\mathrm{fl}} = k\lambda_1\tau_1^A I_1 \exp(-\mu_1 d/\sin\varphi)\exp(-\mu_{\mathrm{fl}} d/\sin\psi), \quad (1)$$

where τ_1^A is the linear absorption coefficient of primary radiation in element A; μ_1 and μ_{fl} are the linear attenuation coefficients of, respectively, primary and secondary radiation in the sample; φ is the angle of incidence of primary radiation on the sample surface; ψ is the take-off angle of the secondary radiation; and k is a coefficient depending on the spectrometer geometry and the sample surface area. Thus, the XRF intensity from the sample surface layer of thickness d can be calculated by the known Blokhin formula [1]:

$$\begin{aligned} I_{\text{fl}} &= k\int_0^d \lambda_1 \tau_1^A I_1 \exp[-M(\lambda_1;\, \lambda_{\text{fl}})d]dx \\ &= k\lambda_1\tau_1^A I_1[1-\exp(-Md)]/M, \end{aligned} \tag{2}$$

where

$$M(\lambda_1;\, \lambda_{\text{fl}}) = \mu_1/\sin\varphi + \mu_{\text{fl}}/\sin\psi. \tag{3}$$

Expansion of the exponential function in a Maclaurin series at $d \longrightarrow 0$ with the use of only the first two terms of the resulting sequence allows us to derive the expression for the XRF intensity of an infinitely thin sample:

$$I_{\text{fl}} = k\lambda_1\tau_1^A I_1 d. \tag{4}$$

For polychromatic primary radiation in the wavelength range from the short-wavelength edge of the X-ray tube emission spectrum (λ_0) to the absorption edge of the element to be determined (λ_q^A), Eq. (4) takes the form

$$I_{\text{fl}} = kd\int_{\lambda_0}^{\lambda_q^A} \lambda\tau^A(\lambda)I_1(\lambda)d\lambda. \tag{5}$$

Applying the generalized theorem of the mean to Eq. (5) makes it possible to calculate the effective wavelength of the fluorescence excitation spectrum for an infinitely thin layer at the surface of the analyte sample:

$$\bar{\lambda}^A_{\text{mono}} = \int_{\lambda_0}^{\lambda_q^A} \lambda\tau^A(\lambda)I_1(\lambda)d\lambda \Big/ \int_{\lambda_0}^{\lambda_q^A} \tau^A(\lambda)I_1(\lambda)d\lambda. \tag{6}$$

For samples of finite thickness, the effective wavelength value is shifted toward shorter wavelengths since the primary radiation is filtered by the surface layers of the sample. Let us estimate this shift. It follows from Eq. (2) that, for a semi-infinite sample, the XRF intensity tends to $I_1/M(\lambda_1;\, \lambda_{\text{fl}})$. Due to absorption in the sample, the intensity of primary radiation changes from I_1 to zero. For a homogeneous sample, the efficiency of this process can be uniquely described using the thickness of the surface layer responsible for half of the XRF intensity at λ_{fl} excited by radiation at λ_1:

$$d_{1/2}(\lambda_1;\, \lambda_{\text{fl}}) = \ln 2/M(\lambda_1;\, \lambda_{\text{fl}}). \tag{7}$$

At $\lambda_1 = \bar{\lambda}^A_{\text{mono}}$, Eq. (7) allows one to calculate the effective thickness of the "filtering layer" of the analyte sample. The transformation of the initial primary radiation spectrum specified as a two-dimensional array $[\lambda_1;\, I_1]$ by Eq. (8) makes it possible to calculate the effective excitation spectrum of element A in a semi-infinite sample:

$$\begin{aligned} I^A_{1,\,\text{eff}} &= I_1\exp\left(-\frac{\mu_1 d_{1/2}(\bar{\lambda}^A_{\text{mono}};\, \lambda_{\text{fl}})}{\sin\varphi}\right) \\ &= I_1\exp\left(-\frac{\mu_1\sin\psi\ln 2}{\mu(\bar{\lambda}^A_{\text{mono}})\sin\psi + \mu_{\text{fl}}\sin\varphi}\right). \end{aligned} \tag{8}$$

Substitution of the effective excitation spectrum intensity for the initial one in Eq. (6) gives the sought effective wavelength of the fluorescence excitation spectrum of the analyte sample. The absorption (attenuation) coefficients are tabulated in a wide range of wavelengths [7].

EXPERIMENTAL

The adequacy of the algorithm for calculation of the effective wavelength was checked in the course of SL XRF analysis of certified steel discs 10 × 4 mm in size. The spectra were measured on a Spektron Spectroscan XRF spectrometer (Russia) equipped with a LiF(200) crystal analyzer ($2d = 0.403$ nm) and a low-power (4 W) sharp-focus X-ray tube with a Mo anode; the working voltage was 40 kV. The angle of incidence of primary radiation was 70° and the take-off angle of secondary radiation was 30°. The Ni, Fe, Mn, and CrK_α lines were used for determination. The optimal exposure time ($s_r < 0.01$) for these elements was 2, 1, 20, and 1 s, respectively. To take into account a possible variation in chemical composition across the sample, the analytical signal was measured four times, turning the sample by an angle of 90°, and the resulting values were averaged.

VERIFICATION OF THE ALGORITHM

Based on the known Blokhin relationship [1], for each jth component of the steel sample, we can write an equation that relates the XRF line intensity to the chemical composition of the analyte (concentrations C_i), the fundamental parameters of the constituting elements of the analyte, and the characteristics of a given spectrometer:

$$a^i_j(C_j/C_{\text{Fe}}) + \sum_{i=1}^{N-2} a^j_i(C_i/C_{\text{Fe}}) = -a^j_{\text{Fe}}, \tag{9}$$

$$a^j_i = \mu^i(\lambda^j_1)\sin\psi + \mu^i(\lambda^j_{\text{fl}})\sin\varphi, \tag{10}$$

$$a^i_j = \mu^j(\lambda^j_1)\sin\psi + \mu^j(\lambda^j_{\text{fl}})\sin\varphi - K^j\sin\varphi\sin\psi, \tag{11}$$

$$K^j = \frac{I^j_{\text{fl}}}{I^j_1}\frac{\lambda^j_{\text{fl}}}{\lambda^j_1}\frac{S^j_q}{S^j_q - 1}\frac{4\pi R^2}{\tau^j_1\omega^j_q p^j_{\text{fl}} s}. \tag{12}$$

Here, N is the total number of components, S^j_q is the jump of the q absorption edge of the jth element, τ^j_1 is the mass absorption coefficient of the jth element with

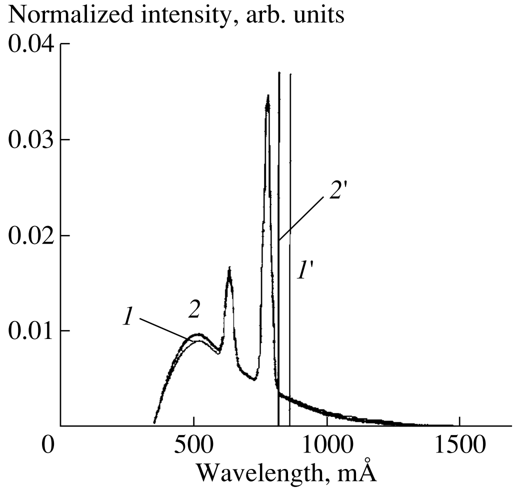

Fig. 1. (*1*) Combined emission spectrum of an X-ray tube and (*2*) effective excitation spectrum of nickel in certified steel no. 93 with normalized integrated intensities in the working wavelength range. The vertical lines (*1*' and *2*') designate the effective wavelengths of nickel excitation calculated in this work (see text for details).

respect to the primary radiation with the wavelength λ_1, ω_q^j is the probability of radiative relaxation of the jth element after the ionization of the q level, p_{fl}^j is the fraction of the analytical line in the total intensity of the q series for the jth element, R is the optical path length from the sample to the detector, and s is the surface area probed by the primary X-ray beam. The λ, μ, τ, ω, and S_q are tabulated [7]. The overall contribution of I_1, R, and s can be determined by measuring the XRF spectrum of any element and by solving the aforementioned Blokhin equation for the corresponding fluorescence line.

Table 1. Calculated effective wavelength of the X-ray tube bremsstrahlung spectrum used for excitation of X-ray fluorescence of elements in certified steel samples*

Element	Effective wavelength, mÅ		
	proposed algorithm	classical approach	
		variant A	variant B
		relative deviation, %	
Steel no. 91			
Ni	1039	895 (–14)	905 (–13)
Fe	1178	1027 (–13)	1035 (–12)
Mn	1252	1103 (–12)	1112 (–11)
Cr	1336	1190 (–11)	1203 (–10)
Steel no. 93			
Ni	1037	895 (–14)	905 (–13)
Fe	1176	1027 (–13)	1035 (–12)
Mn	1250	1103 (–12)	1112 (–11)
Cr	1334	1190 (–11)	1203 (–10)

* See text for details.

The above expressions are valid for a semi-infinite sample excited by monochromatic primary radiation. These equations take into account absorption of primary and secondary radiation in the analyte sample. To calculate the contribution of the additional fluorescence of the analyzed elements excited by the characteristic radiation of the attendant components, the relations derived by Losev [1] can be used. If the contribution of the X-ray tube radiation to the XRF intensity of the jth element is equal to unity, the contribution of the additional excitation by the XRF radiation of the ith element with the wavelength $\lambda_2^i < \lambda_q^j$ is equal to

$$\Delta_2 = \xi \frac{b^i p_2^i \tau_2^j}{\tau_1^j \mu_2} C_i, \quad \text{where } b^i = \frac{\tau_1^i}{2} \frac{S_q^i - 1}{S_q^i} \omega_q^i, \tag{13}$$

$$\xi = \mu_2 \left[\frac{\sin\varphi}{\mu_{1,j}} \ln\left(1 + \frac{\mu_{1,j}}{\mu_2 \sin\varphi}\right) + \frac{\sin\psi}{\mu_{fl}} \ln\left(1 + \frac{\mu_{fl}}{\mu_2 \sin\psi}\right) \right]. \tag{14}$$

Let us formulate the algorithm of SL XRF analysis of steel used in this work.

(1) The elemental composition of a certified steel sample is roughly estimated from the XRF line intensities by the absolute normalization method. Effective wavelengths for all elements are calculated in the first approximation by Eqs. (7) and (8).

(2) The set of linear equations (9) is solved. Concentrations are refined. The effective wavelengths are calculated in the second approximation.

(3) The contribution of additional excitation (13) and (14) is subtracted. The set of equations (9) is solved again to refine the concentrations. The effective wavelengths are calculated in the third approximation.

(4) The final contents of steel components are calculated.

RESULTS AND DISCUSSION

Important factors that determine the effective wavelength are the elemental composition and filtration of the X-ray tube emission spectrum by the surface layers of the analyte sample. Figure 1 shows two spectra with integrated intensities normalized to unity in the range 310–3200 mÅ: the X-ray tube emission spectrum and the effective excitation spectrum of nickel in certified steel no. 93, calculated by Eq. (8). Taking into account the above factors changes by 41 mÅ the effective wavelengths calculated from these spectra by Eq. (6). Table 1 presents the effective wavelengths of compo-

Table 2. Results of standardless X-ray fluorescence analysis of certified steel samples

Element	Content, wt %			Relative deviation, %	
	certificate	calculation (variant 1)	calculation (variant 2)	calculation (variant 1)	calculation (variant 2)
Steel no. 91					
Ni	9.1 ± 0.1	9.9 ± 0.5	9.2 ± 0.4	+9	+1
Mn	0.67 ± 0.02	0.53 ± 0.08	0.59 ± 0.03	–21	–12
Cr	18.0 ± 0.2	15.8 ± 0.6	18.1 ± 0.4	–12	+0.6
Steel no. 93					
Ni	11.1 ± 0.1	12.5 ± 0.4	11.2 ± 0.2	+13	+0.9
Mn	0.36 ± 0.04	0.22 ± 0.06	0.27 ± 0.05	–39	–25
Cr	14.2 ± 0.1	12.9 ± 0.4	14.3 ± 0.3	–9	+0.7

nents of the steel sample calculated by the classical scheme in two variants. The effective wavelength was calculated either as the midpoint of the wavelength range between the short-wavelength edge of the X-ray tube bremsstrahlung spectrum and the absorption edge of the element to be determined (variant A) or as the average of all possible values for an arbitrary analyte (variant B) [1, 5]. This universal approach takes into account only the nature of the analyte and ignores the other factors. As is seen, these values differ considerably from the values calculated by the proposed algorithm. However, in SL XRF analysis, the correctness of the determination of each element depends on the correctness of the determination of all components. Therefore, improper choice of the effective wavelength for only one element can noticeably distort the entire composition. Figure 2 shows the results of numerical estimation of the correctness of the SL XRF analysis of certified steel no. 93 as a function of the choice of the effective wavelength of the combined emission spec-

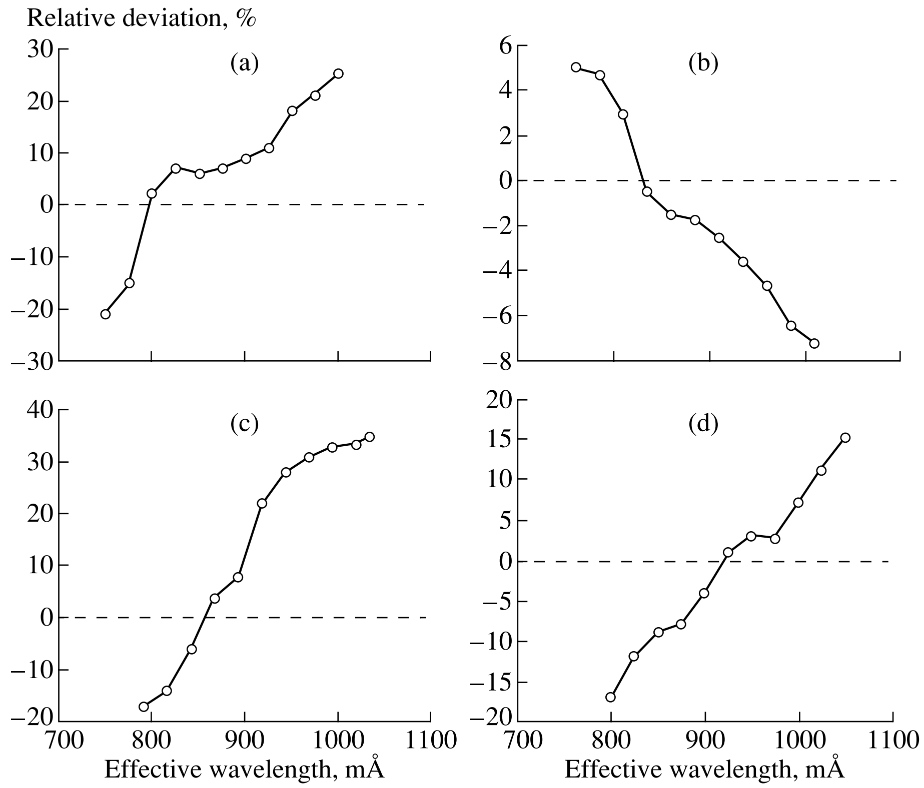

Fig. 2. Relative deviations from the certified values of the results of the SL XRF determination of (a) nickel, (b) iron, (c) manganese, and (d) chromium in certified steel no. 93 as a function of the choice of the effective wavelength of excitation by X-ray tube radiation (numerical estimation).

trum of the X-ray tube. In some cases, the change in the effective wavelength by only 50 mÅ can lead to the change in calculated contents by 5–15%. An additional source of error can be the use of the universal virtual excitation spectrum calculated, for example, by the Kramers equation (variant 1), rather than the real emission spectrum of the X-ray tube of a given spectrometer (variant 2). These spectra were used in the SL XRF analysis of certified steel samples. The correctness of the analysis results is noticeably higher when the effective wavelength of the emission spectrum of a definite X-ray tube is calculated by the algorithm proposed in this work (Table 2). The large relative deviation of the calculated manganese content from the certified value is due to a noticeable spectral overlap of the MnK_α analytical line (2102 mÅ) and the stronger CrK_β line (2085 mÅ).

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