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Excitation of X-Ray Fluorescence of Massive Samples by Bremsstrahlung: Analytical Possibilities of the Monochromatic Model

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Abstract—An algorithm was proposed for calculation of the equivalent analytical wavelength of the bremsstrahlung spectrum during X-ray fluorescence excitation in multicomponent objects of arbitrary thickness. A correlation is found between the analytically obtained approximate values of a given parameter and its exact values found numerically taking into account the design features of an X-ray tube. The approach makes it possible to minimize the error of the results of quantitative X-ray fluorescence analysis of samples of various thicknesses taking into account the matrix effects.

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A characteristic feature of quantitative X-ray fluorescence (XRF) analysis of complex multielement systems is the necessity of consideration of matrix effects. One of such effects is the effect of filtration of the polychromatic emission spectrum of an X-ray tube by the surface layers of an analyte. Due to a strong dependence of the absorption coefficient on the X-ray radiation wavelength and the nature and contents of analytes and matrix components, XRF of deep-seated layers of the sample is excited by primary radiation of a significantly different spectral composition [1]. As a result, the analytical signal intensity turns out to be related not only to the analyte concentration but also to the ratio of the efficiencies of XRF excitation in the control and reference samples. To calculate correction factors taking into account this dependence, an adequate mathematical model is required for describing XRF excitation in massive samples by X-ray tube radiation. The description of this process in the monochromatic approximation is elegant and requires fewer computational resources.

The wave distribution of the polychromatic spectrum of an X-ray tube is replaced by the δ function of a virtual monochromatic source (VMS) of radiation with an analogous excitation effect. All traditional approaches to the determination of the VMS parameters can be divided into two groups. The first group contains the algorithms based on the choice of the so-called effective wavelength (EWL) of primary radiation with the weighted average excitation effect of the XRF of an analyte. Averaging can be both over the wavelengths of the bremsstrahlung spectrum [1] and over the mass absorption coefficients of primary radiation for a sample [2]. Unfortunately, the EWL depends not only on the sample composition but also on the analyte content. Therefore, the error of the results of quantitative XRF analysis is rather high.

More promising from the analytical standpoint are the algorithms belonging to the second group, which are based on the choice of the so-called equivalent wavelength of primary radiation slightly depending on the analyte content. This parameter is calculated analytically with the use of experimentally measured line intensities of two reference samples with compositions limiting the range of expected contents of the analyte element in the control sample [3]. The calculated VMS characteristics ensure an analogous (equivalent) efficiency of XRF excitation for two (rather than for one) samples that differ in the analyte content by one to two orders of magnitude. As a result, the error of XRF determination is considerably lower than when the EWL is used. However, the correctness of the analysis results is limited by the fact that the VMS wavelength is calculated with the use of the universal distribution functions of bremsstrahlung intensity, which ignore the effect of the design features of the X-ray tube of a spectrometer.

The smallest error of the XRF determination results is achieved when an empirical method is used for finding the so-called equivalent analytical wavelength (EAWL) of the experimentally measured spectrum of the X-ray tube [4, 5]. For samples with different analyte contents, the ratio of the fractions of the intensity of the line excited by primary radiation with the EAWL is equal to the ratio of the integrated intensities of this line. Among the drawbacks of this method is the necessity of preparing a large number of reference samples for a wide range of analyte contents, as well as a trial-and-error fitting procedure of finding the EAWL [4].

These drawbacks of the above algorithms, as well as the possibility to analytically calculate the VMS parameters only for thin-film and semi-infinite samples (the two limiting cases) in the absence of interfering elements, led to the increased use of the polychromatic approach to the description of the primary radiation filtration effect. The efficiency of XRF excitation by all components of the X-ray tube spectrum is found by numerical methods [6, 7]. The error of the analysis results is reduced at the cost of considerably complicating the calculations. In this context, a generalization of the monochromatic model to samples of arbitrary composition and thickness that will combine a clear physical meaning, simplicity of calculations, and a low error of the XRF results is an important theoretical and applied problem.

The aim of this study is to derive an approximate analytical formula for calculation of the EAWL of the bremsstrahlung spectrum for samples of various thicknesses and to find correction functions taking into account the design features of an X-ray tube.

THEORY

In the absence of interfering components in a homogeneous semi-infinite sample, the XRF intensity of the ith element excited only by polychromatic X-ray tube radiation is expressed by the Sherman equation [8]

$$I_i = R_i \int_{\lambda_0}^{\lambda_K} \frac{\tau_i(\lambda)}{\mu_s(\lambda)/\sin(\varphi) + \mu_s(\lambda_i)/\sin(\psi)} I_0(\lambda)\, d\lambda, \quad (1)$$

$$R_i = C_i \omega_i f_i (S_K - 1)/S_K, \quad (2)$$

where C_i is the content of the ith element; ω_i is the K fluorescence yield of the ith element; f_i is the contribution of the K_α line to the total intensity of the K series; λ_K and S_K are the wavelength and jump of the K-edge of absorption of the ith element, respectively; λ_0 is the short-wave edge of the bremsstrahlung spectrum; $I_0(\lambda)$ is the primary radiation intensity; $\tau_i(\lambda)$ is the mass absorption coefficient of the ith element for primary radiation; $\mu_s(\lambda)$ and $\mu_s(\lambda_i)$ are the mass attenuation coefficients for primary λ and XRF λ_i radiation, respectively; φ is the angle of incidence of primary radiation on the sample surface; and ψ is the take-off angle of XRF radiation. An analogous equation can be written for the VMS:

$$I_i = R_i \frac{\tau_i(\lambda_{vs}) I_{vs}}{\mu_s(\lambda_{vs})/\sin(\varphi) + \mu_s(\lambda_i)/\sin(\psi)}, \quad (3)$$

where λ_{vs} and I_{vs} are the VMS wavelength and intensity, respectively.

The wave distribution of the X-ray tube is conveniently expressed by the Kramers equation:

$$I_0(\lambda) = k_1 Z_{an} i_c (\lambda - \lambda_0)/\lambda_0 \lambda^3, \quad (4)$$

where k_1 is a constant, Z_{an} is the atomic number of the anode material of the X-ray tube, and i_c is the current density [1]. At $\lambda < \lambda_{K,\,i}$, the mass absorption coefficient (cm^2/g) is

$$\tau_i(\lambda) = 0.016 Z_i^{3.94} \lambda^3 / A_i = p_i \lambda^3, \quad (5)$$

where Z_i and A_i are the atomic number and atomic weight of the ith element, respectively. The mass attenuation coefficient of primary radiation λ can be expressed through the attenuation coefficients of XRF radiation λ_i [1]:

$$\begin{aligned} \mu_s(\lambda) &= (\lambda/\lambda_i)^3 (C_i \mu_i(\lambda_i)(S_K - 1) + \mu_s(\lambda_i)) \\ &= a(\lambda/\lambda_i)^3. \end{aligned} \quad (6)$$

Taking into account Eqs. (4)–(6) and close τ and μ values, we can rearrange Eq. (1):

$$I_i = k_1 Z_{an} i_c p_i R_i (\lambda_i^2 \sin(\varphi)/a\lambda_0) D, \quad (7)$$

$$D = \int_{\lambda_0}^{\lambda_K} \frac{\lambda - \lambda_0}{\lambda^3 + b/a}\, d\lambda, \quad (8)$$

$$b = \lambda_i^3 \mu_s(\lambda_i) \sin(\varphi)/\sin(\psi). \quad (9)$$

An analogous equation can be written for the VMS:

$$I_i = R_i p_i \frac{\lambda_i^2 \sin(\psi)}{a} \frac{\lambda_{vs}^3 I_{vs}}{\lambda_{vs}^3 + b/a}. \quad (10)$$

The VMS intensity is represented as a function of wavelength:

$$I_{vs} = \frac{k_1 Z_{an} i_c}{\lambda_0 \lambda_{vs}^3} (\lambda_{vs}^3 + b/a) D. \quad (11)$$

For a thin-film sample of thickness d and density ρ, the Sherman equation can be rewritten as follows:

$$I_i = R_i \rho d \int_{\lambda_0}^{\lambda_K} \tau_i(\lambda) I_0(\lambda)\, d\lambda. \quad (12)$$

Let us rearrange Eq. (12) taking into account Eqs. (4) and (5):

$$I_i = R_i \frac{k_1 Z_{an} i_c}{\lambda_0} p_i \rho d \int_{\lambda_0}^{\lambda_K} (\lambda - \lambda_0)\, d\lambda. \quad (13)$$

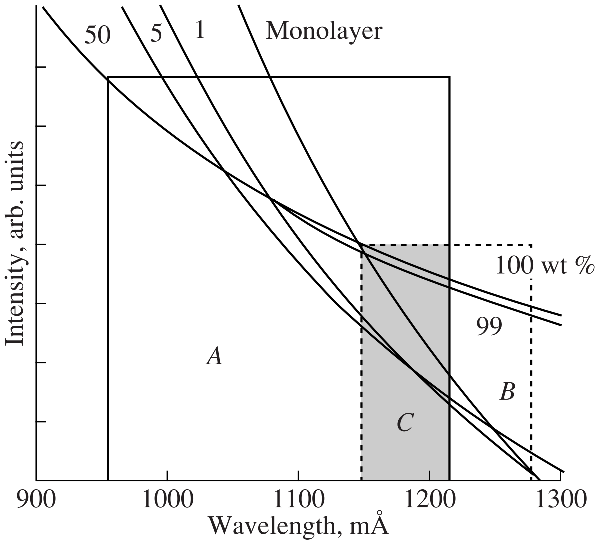

Fig. 1. VMS intensity vs. wavelength for different Fe contents in the Fe–Cr alloy. The anode voltage of the X-ray tube is 45 kV, $\varphi = 35°$; $\psi = 55°$. The equivalent wavelength ranges obtained with variation of (*A*) the analyte element, (*B*) the sample thickness, and (*C*) the EAWL search range are shown.

An analogous equation can be written for the VMS of primary radiation:

$$I_i = R_i p_i \rho I_{vs}\lambda_{vs}^3 d. \quad (14)$$

With the use of Eqs. (13) and (14), the VMS intensity can be represented as a function of wavelength:

$$I_{vs} = \frac{k_1 Z_{an} i_c}{2\lambda_0\lambda_{vs}^3}(\lambda_K - \lambda_0)^2. \quad (15)$$

Equating the right-hand sides of Eqs. (11) and (15), we obtain the formula for the equivalent wavelength of the excitation spectrum of a semi-infinite and thin-film sample:

$$\lambda_Q = \sqrt[3]{(\lambda_K - \lambda_0)^2/2D - \xi}, \quad (16)$$

$$\xi = \frac{b}{a} = \frac{\lambda_i^3}{\gamma(S_K - 1)}\frac{\sin(\varphi)}{\sin(\psi)}, \quad (17)$$

$$\gamma = \frac{Z_i^{3.94}/A_i S_K}{Z_i^{3.94}/A_i S_K + \varepsilon Z_M^{3.94}/A_M}, \quad (18)$$

$$D = \frac{\lambda_0 + \xi}{6\xi^2}\ln\frac{(\xi^2 - \xi\lambda_K + \lambda_K^2)(\xi + \lambda_0)^2}{(\xi^2 - \xi\lambda_0 + \lambda_0^2)(\xi + \lambda_K)^2} + \frac{\xi - \lambda_0}{\xi^2\sqrt{3}}\left[\arctan\frac{2\lambda_K - \xi}{\xi\sqrt{3}} - \arctan\frac{2\lambda_0 - \xi}{\xi\sqrt{3}}\right], \quad (19)$$

where Z_M and A_M are the atomic number and weight of a filler (the matrix components). Once the value of ε (depends on the natures of the analyte and filler) has been adequately chosen, Eq. (16) allows one to calculate the EAWL for samples of arbitrary thickness.

In the presence of interfering elements in the analyte sample, the EAWL determined by an empirical method [4] is sometimes larger than the wavelength of the absorption edge of the analyzed element, which is physically meaningless. Therefore, it is expedient to introduce additional EAWL values for the wavelength segment between the absorption edges of interfering components and between the absorption edges of the interfering (λ_{q1}) and analyte (λ_{q2}) elements. The change in the integration limits in Eqs. (8) and (13) gives the following expression for the EAWL:

$$\lambda_Q = \sqrt[3]{(\lambda_{q2} - \lambda_{q1})\left(\frac{\lambda_{q2} + \lambda_{q1}}{2} - \lambda_0\right)/D_{IE} - \xi_{IE}}, \quad (20)$$

$$D_{IE} = \int_{\lambda_{q1}}^{\lambda_{q2}}\frac{\lambda - \lambda_0}{\lambda^3 + \xi_{IE}}d\lambda, \quad (21)$$

The rearrangement of Eq. (20) and the variable transformation

$$\lambda_Q = (\lambda_{q2} + \lambda_{q1})/2 \quad (22)$$

give the identity that is the mathematical expression of the first mean-value theorem for definite integral (21):

$$\int_{\lambda_{q1}}^{\lambda_{q2}}\frac{\lambda - \lambda_0}{\lambda^3 + \xi_{IE}}d\lambda \equiv (\lambda_{q2} - \lambda_{q1})\frac{\lambda_Q - \lambda_0}{\lambda_Q^3 + \xi_{IE}}. \quad (23)$$

A more correct wave distribution of the bremsstrahlung intensity of the X-ray tube can be calculated by the formula [9]

$$I_0(\lambda) = k_2 Z_{an}\frac{\lambda - \lambda_0}{\lambda_0^{1+a}\lambda^{2-a}}\ln^{-1}\left(\frac{1166(2E_0 + E_\lambda)}{3J}\right) \times R_\lambda f_\lambda \exp(-\mu_\lambda^{Be}\rho_{Be}d_{Be}), \quad (24)$$

where k_2 is a constant; a is a parameter depending on Z_{an}; E_0 and E_λ are the electron and bremsstrahlung photon energies (keV), respectively; $J = 11.5Z_{an}$ is the average ionization potential of anode atoms (eV); R is the backscattering factor of electrons in the anode [10]; μ^{Be} is the mass attenuation coefficient of the Be window; ρ_{Be} is the beryllium density; and d_{Be} is the Be window thickness. The Philibert absorption correction (mass coefficient μ^{an}) is

$$f_\lambda = (1 + \mu_\lambda^{an}\sigma_\lambda^{-1}\sin^{-1}\psi)^{-1}(1 + h\mu_\lambda^{an}\sigma_\lambda^{-1}\sin^{-1}\psi)^{-1}, \quad (25)$$

Table 1. Calculated (1) and empirical (2) EAWL values (mÅ) for different elements (the X-ray tube anode voltage, 45 kV; $\varphi = 35°$; $\psi = 55°$)

Algorithm	Element			
	^{26}Fe	^{30}Zn	^{40}Zr	^{50}Sn
^{24}Cr filler				
1	1181	939	539	367
2	1188	946	545	375
^{16}S filler				
1	1148	921	534	367
2	1139	915	535	370

in a massive anode and

$$f_\lambda = \frac{\exp(-\mu_\lambda^{\mathrm{an}}\rho_{\mathrm{an}}d_{\mathrm{an}})(1-h) - \exp(-\sigma_\lambda\rho_{\mathrm{an}}d_{\mathrm{an}})}{(1-\mu_\lambda^{\mathrm{an}}/\sigma_\lambda)(1-h-\exp(-\sigma_\lambda\rho_{\mathrm{an}}d_{\mathrm{an}}))},$$
$$h = \frac{1.2A_{\mathrm{an}}/Z_{\mathrm{an}}^2}{1+1.2A_{\mathrm{an}}/Z_{\mathrm{an}}^2}, \tag{26}$$

in a thin-film anode. Here, ψ is the take-off angle of anode radiation; A_{an}, ρ_{an}, and d_{an} are the atomic weight, density, and thickness of the anode; and σ is the electron energy loss factor

$$\sigma = 4\times10^5/(E_0^{1.65} - E_\lambda^{1.65}). \tag{27}$$

This procedure was used in this work for numerical calculation of the VMS wavelength corrected for the design features of the X-ray tube.

EXPERIMENTAL

To verify the validity of the suggested algorithm, we determined the contents of Zn and Ni in certified specimens of aluminum alloy and steel (metallic cylinders ∅12 × 4 mm in size with a polished surface) by the external reference method with corrections for absorption. The spectra were measured on a Spektron Spectroscan-G Max series XRF spectrometer (Russia) equipped with a low-power (4 W) sharp-focus (∅1.5 mm) X-ray tube with a Cr anode. The working voltage and current were 40 kV and 100 μA, respectively. The angle of incidence of primary radiation was 80° and the take-off angle of secondary radiation was 30°. A LiF (200) crystal analyzer ($2d = 4028$ mÅ) was used for converting secondary radiation to a wave spectrum by the Johansson method. For detection of secondary X-ray quanta, the spectrometer was equipped with a sealed gas-discharge proportional counter.

The contents of Zn and Ni were determined from the ZnK_β (1295 mÅ) and NiK_β (1500 mÅ) line intensities. The exposure time was 10 s (the counting rate was above 5000 counts/s). Corrected spectral line intensities were found by measuring the amplitude distribution of the XRF intensity of the analyte element with a step of 2 mÅ and the continuous spectral component intensity in the vicinity of the characteristic peak (±50 mÅ) followed by correction of the background signal. The VMS parameters were calculated by Eq. (16) and by common methods [1–4].

RESULTS AND DISCUSSION

In this work, a correlation between the VMS intensity and wavelength was established for a wide range of iron contents in the Fe–Cr alloys (Fig. 1). The abscissas of the intersections of these curves (the VMS equivalent wavelengths for two semi-infinite samples) are distributed over the range 953–1219 mÅ, and EAWL is 1086 mÅ. The error of determination of iron (1–50 wt %) changes from +2.2 to –1.4%. The abscissas of the intersections of the curves with the thick line (the VMS equivalent wavelength for thin-film and semi-infinite samples) are distributed over the range 1152–1282 mÅ. When the corresponding EAWL (1181 mÅ) is used, the error of determination of iron in a wide range of contents changes from +0.36 to –0.29%. Thus, the number of possible VMSs of primary radiation is infinitely large. However, no VMS exists that has truly composition-independent parameters. The equivalent wavelength suggested in [3] is a result of optimization of the VMS parameters for the studied range of analyte contents in a semi-infinite sample. The algorithm

Table 2. Relative error (%) of the results of quantitative XRF analysis of certified metal alloys

Element (content, wt %)	Concomitant components	Algorithm for calculation of VMS parameters				
		[1]	[2]	[3]	[4]	(16)
Steel sample						
Ni (6.71)	Fe, Mn, Cr, Ti	6.6	5.8	3.7	1.3	1.3
Duralumin sample						
Zn (8.87)	Zr, Cu, Ti, Si	5.2	4.7	2.5	1.4	1.4

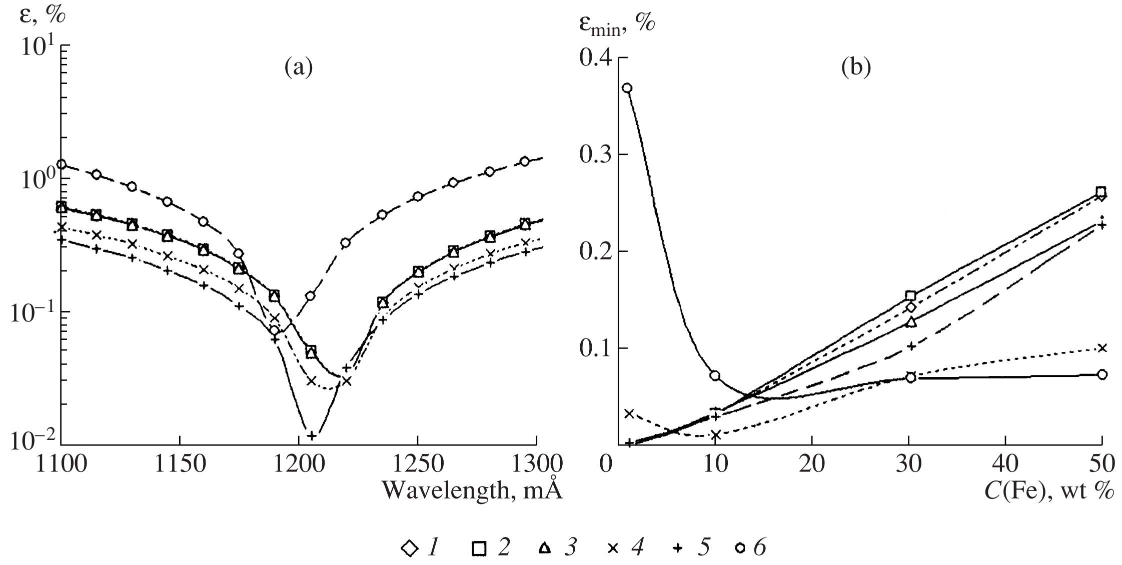

Fig. 2. (a) Relative error of determination of iron in the Fe–Cr alloy vs. VMS wavelength (the VMS parameters were calculated for *C*(Fe) = 10 wt %) and (b) the minimal relative error of determination on the iron content used for calculating VMS parameters. The sought iron content (wt %): (*1*) 0.1, (*2*) 0.3, (*3*) 1.0, (*4*) 3.0, (*5*) 10, and (*6*) 30. The anode voltage of the X-ray tube is 45 kV, φ = 35°; ψ = 55°.

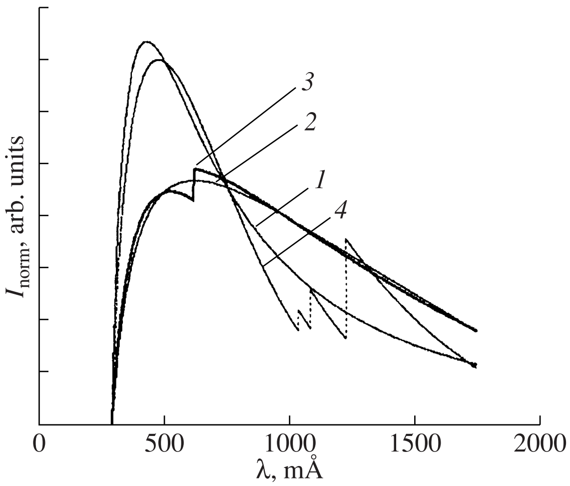

Fig. 3. Wave distributions of (*1*) the bremsstrahlung intensity calculated by the Kramers formula and for the end-window X-ray tube with a thin-film (2 μm) (*2*) Cr, (*3*) Mo, and (*4*) W anode (working voltage, 45 kV).

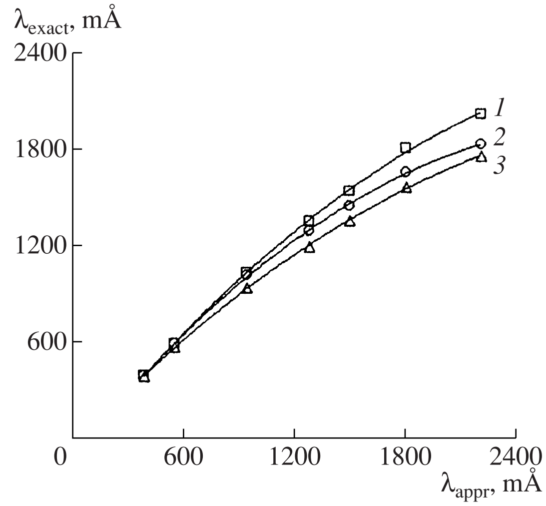

Fig. 4. Correlation between EAWL (λ_{exact}) of the bremsstrahlung spectrum of an end-window X-ray tube with a thin-film anode of a thickness of (*1*) 1, (*2*) 10, and (*3*) 100 μm (λ_{appr}) found by formula (16) for a semi-infinite sample with a density of 9 g/cm^3.

expounded in this work allows one to optimize the equivalent wavelength values for samples not only of different composition but also of different thickness. The minimal error is achieved in analysis of a semi-infinite sample with the use of a reference thin-film sample of known density and thickness, as well as when both samples are nonsaturating emitters of the same thickness.

The dependence of the analysis error magnitude on the VMS wavelength has an extreme point near the EAWL. Figure 2a shows examples of such V-shaped curves for different iron contents in the Fe–Cr alloy. Figure 2b shows the smallest error of analysis with the use of several $I_{vs}(\lambda_{vs})$ functions calculated for different iron contents in the Fe–Cr alloy. The optimal content of an element for calculation of $I_{vs}(\lambda_{vs})$ is within 10–30 wt %, i.e., $\varepsilon \in [3, 9]$. The exact value depends on the nature of the analyte element and the filler. In most cases, ε = 4 in Eq. (18) can be successfully used in practice.

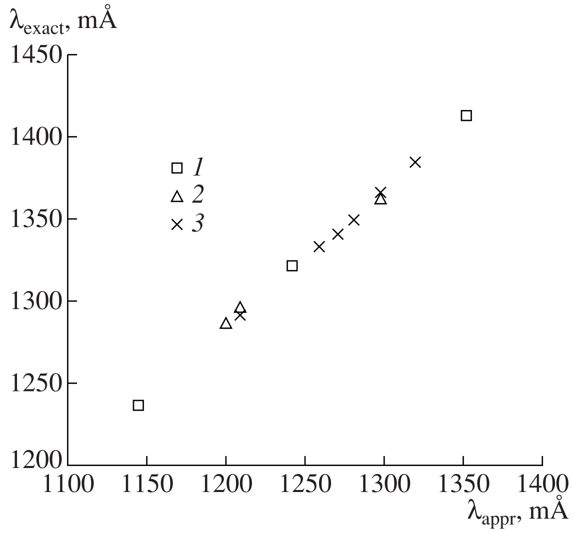

Fig. 5. Correlation between the EAWL values calculated for the bremsstrahlung spectrum of an end-window X-ray tube with a thin-film (2 μm) anode (λ_{exact}) and found by formula (16) (λ_{appr}) when only one parameter is varied: (*1*) the nature of the analyte element, (*2*) the matrix composition of the sample, and (*3*) the X-ray tube voltage (20–60 kV).

For a wide range of analyte elements in various matrices in the absence of interfering components, the EAWL values found empirically and calculated by Eq. (16) are very close (Table 1). The deviation of the results of quantitative XRF analysis is no more than a few tenths of a percent (Table 2). In the general case, there is a simple relationship between the approximate EAWL values analytically calculated by Eq. (16) and the exact values numerically found from the bremsstrahlung spectra of real X-ray tubes (Fig. 3) and samples of variable thickness and density; this relationship is approximated by a parabolic function with a correlation coefficient no worse than 0.98. Examples of such a relationship are shown in Fig. 4. This dependence remains valid when the anode material (Cr, Mo, W) and thickness (from 2 μm to ∞) and the thickness of the beryllium window of an X-ray tube (75–300 μm) are varied simultaneously. For each analyte element ($Z = 11–50$), when only one experimental parameter—the matrix composition of a sample, its density (2–10 g/cm^3), or working voltage on the electrodes of an X-ray tube (20–60 kV)—is varied, the correlation becomes linear (Fig. 5)! Thus, correction of approximate EAWL values taking into account specific features of the wave distribution of bremsstrahlung of an X-ray tube with a thin-film or massive anode is not a difficult problem.

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