

Compensation of Roentgen Exciting System Instability in Conducting X-Ray Fluorescence Analysis of Bioassays

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Detailed analysis of the backscattering peak in the X-ray fluorescence spectrum was carried out using the Monte Carlo method which is the base of the computer code "SNEGMONT" for simulating the transport of electrons and photons. The calculations show that the intensity of the backscattering peak is directly proportional to the intensity of the exciting radiation. It was found that the intensity of analyzed elements' lines has a strict relation with the intensity of the backscattering peak. The example of determination of lead and zinc concentrations in bioassay is presented. The simulation of an eightfold change of the exciting X-rays intensity which taking into account the obtained strict relation allows to determine the true concentration of elements with an error of no more than 3%.

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1. Introduction

Determination of the actual content of trace elements in blood, urine and hair is the subject of intensive scientific research in clinical practice [1–5]. X-ray fluorescence (XRF) method has a special place [6–15] among the existing methods of the quantitative determination of the microelement composition of bioassay [15–20].

Nondestructive testing, analysis of bioassay without prior sample preparation, analysis quickness, a wide range of determined elements (from boron to uranium) and their quantities (from 100 to 10^{-4} wt%) as well as the possibility of simultaneous analysis of the entire spectrum of trace elements which allows to avoid errors in their relations, should be included in the advantages of XRF analysis.

Nowadays a material and methodological basis for performing X-ray fluorescence analysis of bioassay exist. These are portable X-ray fluorescence spectrometers with high sensitivity and resolution, and techniques of measurement in these devices which are approved by the Ukrainian Ministry of Public Health.

Characteristic X-ray emission line of element carries information about its absolute content in the sample at the quantitative X-ray fluorescence analysis of microelement composition of bioassay. The intensity of this line of element depends on the concentration of particular element in the sample and the intensity of the exciting

X-rays at actual conditions of X-ray fluorescence analysis. The latter value depends mainly on the X-ray tube current [21].

In practice, the quantum loading of the exciting radiation can vary by 10–20% during a single measurement. It depends on an uncontrolled work specifics of the X-ray exciting system, the ambient temperature and line voltage instability. Such instability of the X-ray exciting system during the measurement makes the largest contribution to the error of the determination of the bioassay microelement composition.

Therefore, the purpose of this study was to find the way to compensate the initial X-rays emission fluctuations, using the characteristics of the obtained X-ray spectra.

2. Backscattering peak

Analysis of the measured X-ray fluorescence spectrum from the organic matrix (Fig. 1) shows that together with the characteristic lines of elements there is also a broad backscattering peak (BP) of the initial exciting X-radiation, which occupies the area from 16 to 32 keV.

Detailed analysis of the backscattering peak in the X-ray fluorescence spectrum was carried out using the Monte Carlo method which is the base of the computer code "SNEGMONT" for simulating the transport of electrons and photons [22]. Program "SNEGMONT" allows us to solve problems associated with modeling the ionizing radiation transport through the complex chemical composition environment in real three-dimensional geometry.

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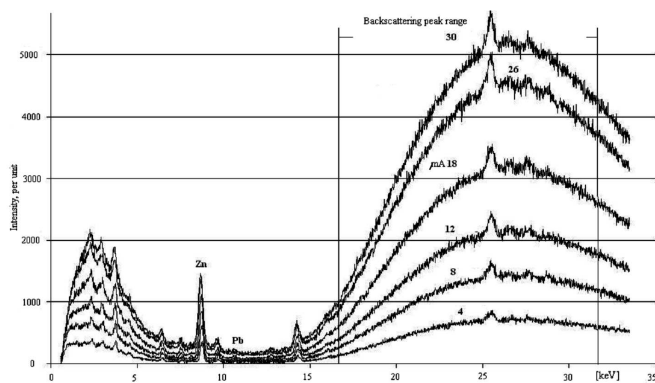


Fig. 1. Characteristic X-ray fluorescence spectra of the NCS DC73347 sample at different values of the X-ray tube current.

The Rayleigh and Compton scattering of photons, photoabsorption and fluorescence, ionization of atoms by electron impact, the relaxation of electronic shells with the generation of fluorescence photons and the Auger electrons, as well as bremsstrahlung of electrons and positrons and the formation of electron-positron pairs and annihilation of positrons are modeled. Photon part of software is the database created on basis of known tested sources, additionally tested and converted to a form suitable for using in Monte Carlo simulation. Cross-sections for the Rayleigh and Compton scattering of photons are given in respect of the influence of the atomic structure on them [23]. As for the photoelectric absorption, the ionization not only of K -, L - and M -shells is described by the corresponding partial cross-sections, but also all the shells which exist in the atoms of each concerned element (even americium). It allows to model the generation and escape of all possible photoelectrons and the formation of all possible inner core holes. The database contains information needed to simulate the relaxation of inner core holes accompanied with the fluorescence, the Coster-Kronig transitions and the emission of the Auger electrons. The geometric unit in the code allows to simulate the structure of complex technical devices, instruments and natural objects. At the same time their relative positions, joining, nesting and penetration between geometric modules (parallelepipeds, cylinders, ellipsoids, cones, etc.) are saved.

X-ray spectra of the exciting radiation from the tungsten anode X-ray tube with titanium filters (see Fig. 2) and the response functions of the detector XR-100 installed in the X-Ray fluorescence spectrometer "Elvax" were calculated using the "SNEGMONT" code. The initial parameters of the spectrometric system used in the calculations are presented in Table I. The calculation was performed in two steps. Spectrum of the photon radiation generated by tube after passing through the Be-window and titanium filter was calculated at the first step. At the second step, the obtained spectrum was the initial spectrum of X-ray beams directed into the sample.

TABLE I

Parameters of the spectrometric system "Elvax".

Exciting device	
X-ray tube	W-anode, Be-window (thickness 250 μm), self-cooling
generator	voltage 45 keV, current 18 μA , power 5 W
stability	0.1% over 8 h continuous work
Detector of X-rays	
type of Roentgen detector	XR-100, semiconductor Si-PIN with thermoelectric cooling
active area of crystal	7 mm^2
entrance window	Be-window (thickness 25 μm)
resolution	up to 180 V at the line of 5.9 keV (isotope Fe^{55})

TABLE II

The energy position of the maximum intensity of X-ray tube spectrum for various thicknesses of titanium filter.

Ti thickness [μm]	Energy position [keV]
400	32.1
300	30.2
200	27.1

Calculations showed that the number of decelerated electrons on a tungsten anode X-ray tube with a current 1 μA corresponds to 6241×10^9 electrons/s. Position of the maximum intensity of the output radiation of X-ray tube depends on the thickness of the titanium filter (Table II). The spectrum is bell-shaped in the 12–45 keV range and has narrow peaks with energy of 4.5 and 4.9 keV that corresponds to the K_α and K_β characteristic emission lines of titanium (Fig. 3). It is clear that the absolute value (photons/ 10^9 electrons) in the emission spectrum of the tube will increase with the increase of tube current.

The scheme which is presented in Fig. 4 was used for calculations of the response function of energy-dispersive detector XR-100 on the initial radiation of X-ray tube (Ti-filter, the thickness of 400 μm , tube current 18 μA , voltage 45 keV) after passing through the teflon sample

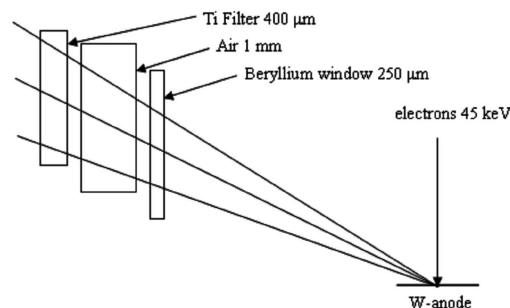


Fig. 2. Design model of X-ray tube with tungsten anode.

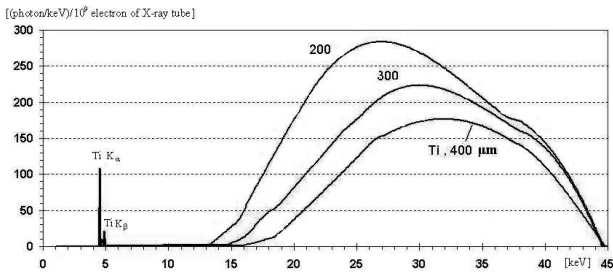


Fig. 3. Calculated spectra of X-ray fluxes that emerge from the X-ray tube with titanium filters of different thickness.

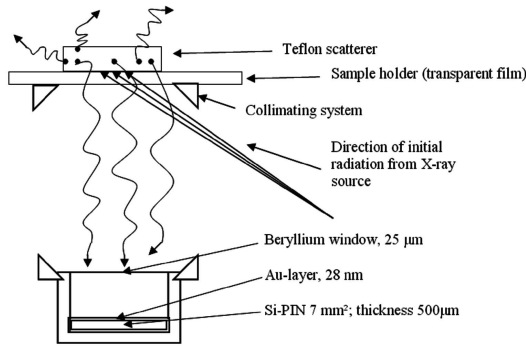


Fig. 4. Scheme of X-ray detector XR-100 and scattering teflon disk.

(diameter is 10 mm, thickness 0.5 mm, weight 49 mg). The choice of teflon disk is justified by the fact that the chemical composition of teflon does not contain heavy elements and therefore is an ideal object for modeling experiments. The simulated response function of the X-ray detector on the initial radiation after scattering at the teflon disk in comparison with the experimental spectrum is shown in Fig. 5. Some differences in the shape of the calculated and experimental spectra are caused by inaccurate representation of initial geometrical and ma-

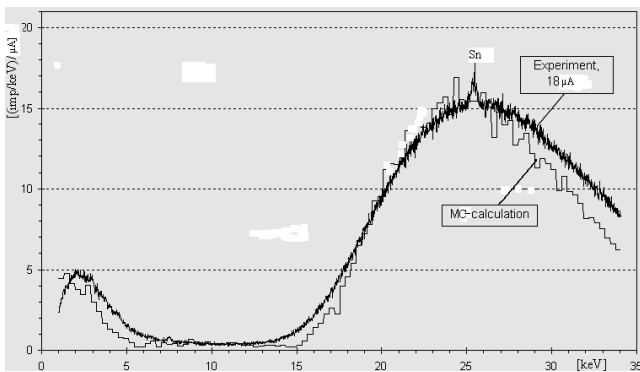


Fig. 5. The simulated and experimental response functions of the XR-100 detector on the initial radiation after scattering at the teflon disk.

terial parameters in the computational model. The peak of 25 keV in the experimental spectrum originating from the presence of tin in the construction of the detector collimator. The presence of tin was not considered in the model. The more detailed studies showed that a broad peak in the range from 1 to 5 keV is created by the effects of the Compton radiation output through the upper and lower edge of the detector. The performed calculations show that the intensity of the backscattering peak (BP) is directly proportional to the intensity of the exciting radiation. This allows us to estimate the integral quantum loading, which got a sample during the measurement.

3. Material and measurement procedure

3.1. Preparation of samples and their analysis

Hair sample NCS DC73347 (with weight 54 mg) was used as a test bioassay. This sample has known concentration of Pb and Zn ($C_{Pb} = 7.0 \pm 1.1 \mu\text{g/g}$ and $C_{Zn} = 120 \pm 9 \mu\text{g/g}$) [24]. Calibration factors for conversion of elements characteristic lines intensities into their weight content [mg] were determined by the X-ray fluorescence spectrometer “Elvax” with the tube current $18 \mu\text{A}$ and the voltage 45 keV. The test sample was measured at the different currents of X-ray tube (from 4 to $30 \mu\text{A}$), thereby modeling an eightfold change of the exciting X-rays intensity. Comparative graph of the obtained spectra is shown in Fig. 1. It is clear that the intensities of backscattering peak and characteristic lines for lead and zinc rise as the current tube increases.

3.2. Results and discussion

Analysis of the measured spectra (Fig. 1) showed that the intensity of characteristic elements’ lines has a strict relation with the intensity of the backscattering peak. The results of the determination of this relation are shown in Fig. 6, where the intensity of Pb L_{α_1} line nor-

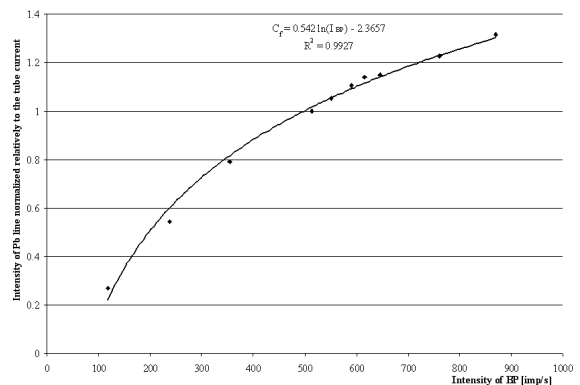


Fig. 6. The dependence of the normalized Pb L_{α_1} line intensity on the BP intensity.

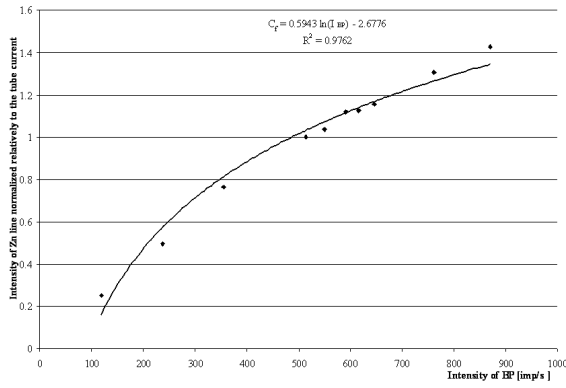


Fig. 7. Dependence of the normalized to the tube current intensity of Zn peak on the BP intensity.

malized relatively to the tube current is shown in function of the intensity of the BP measured as the area under the BP normalized to the time of the measurement. The

found dependence is interpolated by logarithmic function

$$C_f = 0.542 \ln(I_{BP}) - 2.3657.$$

In this dependence $C_f = \frac{I_{Pb}}{I_{Pb(18 \mu A)}}$ is the correction factor, where $I_{Pb(18 \mu A)}$ is the intensity of lead analytical line measured with the optimal parameters of X-ray tube. The calibration coefficients were determined at these optimal parameters. Applying this relation it is possible to calculate the intensity of analytical lines at the optimum parameters for any value of the BP intensity, i.e.

$$I_{Pb(18 \mu A)} = \frac{I_{Pb}}{C_f}.$$

Then the true content of lead in the sample is calculated using the known calibration coefficients, and knowing the mass of the sample you can calculate its concentration. Similar dependence was obtained for zinc (see Fig. 7). The calculated values of peak intensity and concentration of lead and zinc are listed in Table III. Absolute weight and concentration of these elements in the sample were calculated applying the C_f (see Table III).

Calculated values of BP intensity, Pb L_{α_1} and Zn K_{α_1} lines intensity, their absolute weight and concentration.

TABLE III

Tube current μA	BP intensity [imp/s]	Intensity of Pb peak [imp/s]	Absolute weight of Pb (subject to the C_f) [μg]	C_{Pb} $\mu g/g$	Intensity of Zn peak [imp/s]	Absolute weight of Zn (subject to the C_f) [μg]	C_{Zn} $\mu g/g$
4	118.689	0.255	0.392	7.254	4.168	6.796	125.866
8	237.487	0.517	0.375	6.937	8.232	6.335	117.329
12	354.667	0.750	0.355	6.566	12.662	6.378	118.119
18	513.719	0.950	0.356	6.599	16.608	6.550	121.312
19	550.517	1.000	0.363	6.724	17.202	6.457	119.587
20	591.250	1.050	0.371	6.866	18.577	6.555	121.394
21	615.722	1.083	0.378	7.000	18.733	6.523	120.810
22	645.554	1.092	0.379	7.012	19.215	6.468	119.789
26	761.597	1.167	0.369	6.841	21.702	6.528	120.898
30	869.742	1.250	0.374	6.934	23.737	6.463	119.702
average value			0.371	6.873		6.505	120.481
standard deviation			0.011	0.206		0.124	2.314
relative error%			2.992	2.992		1.920	1.920

4. Conclusions

The simulation of the BP in the X-ray characteristic spectrum for different thicknesses of titanium filter was performed with the help of the Monte Carlo method that is the basis of the computer code "SNEGMONT" which models the transport of electrons and photons. It is shown that the intensity of the exciting radiation in the BP has a proportional dependence on the current of X-ray tube. The response function of the detecting system based on Si-PIN detector XR-100 in the geometry of the applied X-ray fluorescence spectrometer "Elvax" was also calculated. Sufficiently good agreements between experimental and theoretical scattering spectra

for the model matrix of teflon disk are obtained. The functional relation between the intensities of the characteristic lines of elements and the intensity of the BP was experimentally estimated. It is shown that the intensities of analytical lines of lead and zinc are 5 times greater (500%) if we change the current of X-ray tube almost 8 times. Applying the correction factor (C_f) of the X-ray exciting radiation fluctuations we demonstrated that the relative error of the estimated concentration for Pb is less than 3%, and for Zn is less than 2%.

References

- [1] A.V. Kudrin, O.A. Gromova, *Microelements in Immunology and Oncology*, GEOTAR-Media, Moscow 2007.
- [2] M. Zimmermann, *Microelements in Medicine* (by Burgerstein), Arnebiya, Moscow 2006.
- [3] A.P. Avtsyn, A. A Zhavoronkov, M.A. Rish, L.S. Strochkova, *Human Microelement Deficiency: Etiology, Classification, Organ Pathology*, Meditzina, Moscow 1991.
- [4] A.I. Voynar, *Biological Role of Microelements in the Organism of Animals and Humans*, Vysshaya shkola, Moscow 1960.
- [5] L.R. Nozdryuhina, *Biological Role of Microelements in the Organism of Animals and Humans*, Nauka, Moscow 1977.
- [6] Dj. I. Djaparidze, N.V. Shavgulidze, N.S. Havtasi, L.G. Enukidze, I.Z. Harischarishvili, E.K. Kirilenko, S.N. Galchenko, *Ukr. J. Occupat. Health* **2**, 58 (2008).
- [7] T.A. Kupriyanova, O.I. Lyamina, V.F. Semenov, *J. Clinical Laboratory Diagnosis* **8**, 11 (1999).
- [8] M. Szczerbowska-Boruchowska, *J. X-ray Spectrom.* **37**, 21 (2008).
- [9] V.I. Fedorov, *J. Clinical Laboratory Diagnosis* **4**, 8 (2006).
- [10] N.F. Losev, A.N. Smagunova, *Fundamentals of X-ray Fluorescence Analysis*, Khimiya, Moscow 1982.
- [11] A.I. Obukhov, O.I. Plekhanova, *Atomic Absorption Analysis in Soil — Biological Research*, Izdatel'stvo Moskovskogo Universiteta, Moscow 1991.
- [12] N.N. Petrova, N.P. Makarenko, T.K. Kachalkova, L.A. Khazemova, *J. Med. Work Industr. Ecology* **3**, 35 (2000).
- [13] E.G. Chudinov, *Atomic-Emission Analysis with Inductively-Coupled Plasma*, Vol. 2, VINITI, Moscow 1990.
- [14] I. Rodushkin, F. Odman, R. Olofsson, M. Axelsson, *J. Anal. At. Spectrom.* **15**, 937 (2000).
- [15] J. Begerov, M. Turflend, L. Dunemman, *J. Anal. At. Spectrom.* **12**, 1095 (1997).
- [16] E.E.M. Brouwers, M. Tibben, H. Rosing, J.H.M. Schellens, J.H. Beijnen, *Mass Spectrom. Rev.* **27**, 67 (2008).
- [17] V.V.S. Ramakrishna, Vivek Singh, A.N. Garg, *J. Sci. Total Environ.* **192**, 259 (1996).
- [18] L.I. Zhuk, A.A. Kist, *J. Radioanal. Chem.* **195**, 75 (1995).
- [19] E.A. Osipova, *Soros Educat. J.* **2**, 47 (2000) (in Russian).
- [20] G. Fridman, *Usp. Fiz. Nauk* **87**, 675 (1965) (in Russian).
- [21] N. Sasaki, K. Okada, J. Kawai, *J. X-ray Spectrom.* **39**, 328 (2010).
- [22] G.A. Fokov, G.I. Shul'govich, *Spectrometric Analysis. Equipment Data Proc. PC* **1**, 145 (2008) (in Russian).
- [23] S.V. Podolyako, E.G. Luk'yanova, *The account of influence of forms factors on angular distribution of photons at numerical modeling transformations of X-ray radiation in objects*, KIAM Preprint 6, Moscow 2004 (in Russian).
- [24] Certificate of Certified Reference Materials NCS DC 73347 — NCS DC 73351/ Approved by China National Analysis Center for Iron and Steel, 2004.