

The X-Ray Fluorescence

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Abstract

The fluorescence of X-rays is a non-destructive method used for the qualitative and quantitative elementary composition determination of the sample with different number of elements. The main advantage of the analysis of the fluorescence radiation from the X-rays area consists in the simplicity of this spectrum. The vacationing of the deep electronic levels of the atoms is followed by the appearance of the phenomenon of X-ray fluorescence. These phenomena depend on the mechanism where the electronic vacancies are created in the deep electronic levels of the atoms, depending on the atomic number of element Z. This method can be used without restrictions to the dosage for all elements from the periodic table with $Z > 12$.

Key words: X-ray fluorescence, XR, Moseley law, isotopic sources

The Intensity of the Fluorescence Radiation

The quantity, which characterizes the intensity of the fluorescence radiation, is the efficaciousness of fluorescence, defined by the ratio of the number of the vacancies from the energetic level that suffer deexcitations with emission of fluorescence radiation and the number of the total vacancies produced by the incident radiation. The semi-empirical relation of the efficaciousness of fluorescence of radiations X is

$$w_z = 0,957 Z^4 / (0.984 + Z^4), \quad (1)$$

with Z the atomic number of the analyzed element.

The physical processes that determine the intensity of the radiation of fluorescence of the element are:

- the absorption of the incident radiation;
- the emission of the fluorescence radiation having energy ε_i ;
- the absorption of this energy by other elements from the sample;
- the secondary emission of the fluorescence radiations by the elements from the sample with Z having a more reduced value than for the dosed element.

The determination of the intensity of the fluorescence radiation depends on the concentration of the emissive element. Mass attenuation coefficients for the incident radiation and for the fluorescence radiation are determined by the radiation energy and the atomic number Z of the elements that compose the sample given $\mu_{m_i}(\varepsilon)$ and $\mu_{m_k}(\varepsilon_k)$ (k is referred to the k order element from the sample).

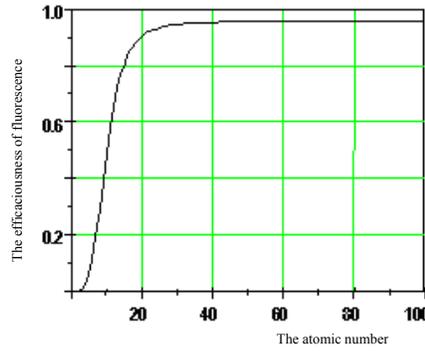


Fig. 1. The efficaciousness of fluorescence depending on the atomic number

Because the energy of the fluorescence radiation is dependent on the measure geometry, the detector of radiations must protect only against the action of the excitation radiation.

Considering a layer, with dx thickness in the sample, d at depth x from the sample surface, therefore the intensity of a primary radiation that reaches this layer is

$$I_x = I_0 \exp\left[-\frac{\mu(\varepsilon)\rho x}{\cos\varphi}\right], \quad (2)$$

where φ is the incidence angle of the excitation radiation. The fluorescence radiation intensity with energy ε_i , emitted by the considered layer of material is

$$dI_{i,1} = w_i \frac{\mu_i(\varepsilon)}{\cos\varphi} \rho c_i I_0 \exp\left[-\frac{\mu_i(\varepsilon)\rho x}{\cos\varphi}\right] dx. \quad (3)$$

The fluorescence radiation ε_i shall be excited also by one from the element j that was produced by the incident radiation. The condition for this process to be effective is $\varepsilon_j > \varepsilon_i$ and its contribution is $dI_{i,2}$ dependent on the concentration of element i . Up to the exit to the sample surface it is presupposed that both components of radiation, primary and secondary fluorescence, should suffer only an attenuation process, resulting in

$$dI_i = (dI_{i,1} + dI_{i,2}) \exp\left[-\frac{\mu(\varepsilon_i)\rho x}{\cos\psi}\right], \quad (4)$$

with ψ , the orientation angle of the detector axis. Taking into account the limits of integration concerning the solid angle below that the detector is seen, the thickness of the sample and the supplementary simplifier conditions the integration output drives to

$$I_i = k c_i (1 + \beta c_i). \quad (5)$$

In this relation k and β are coefficients that depend on the mass attenuation coefficients and the efficaciousness of fluorescence. Represents as is observed the intensity of the fluorescence radiation has a nonlinear dependency on the concentration of the emitting element, nonlinearity that is due to the complex influence of other elements from the sample.

These elements consist in a “matrix” connected to the element i that must be dosed. The elimination of the matrix effects represents one of the main problems of the X-ray fluorescence. Relation (5) was established due to the exciter source monochromaticity. If the exciter source is polychromatic, for the solution of the problem we must take into account of for the spectrum form.

Matrix Effects

For binary mixtures in which the matrix element (appointed also diluent) has an atomic number much more than of an element dosed, the matrix effects are neglected (example: the dosage of the lead in gasoline). The matrix effects can be grouped into two categories:

- The impoverishment effects appear when the element or elements that must be dosed are found in a matrix, with major Z and the energy of the excitation radiation has a value closer to the energy of the fluorescence radiation. The incident radiation shall excite merely the fluorescence radiation while the matrix elements shall supplementary absorb the fluorescence radiation. The effect is more pronounced with the greater difference between the dosed elements atomic numbers Z and the atomic numbers for elements that compose the matrix.
- The enrichment effects appear in the case when the energy of the excitation radiation is bigger than the energy of the fluorescence radiation for the investigated elements. The elements that compose the matrix, consist in heavy elements and they, emit very intense fluorescence radiations. These intense fluorescence radiations shall overlap across one of the dosed elements causing a growth of the fluorescence signal produced by the dosed elements.

Practically, the two effects could appear simultaneously, and their compensation / correction is a fundamental problem of X-ray fluorescence.

Methods for the Elimination of the Matrix Effects

The sample preparation consists of addition of a reference. The addition can be unique or multiple and consists of the addition of precisely determinated amounts from the element (or the elements) that must dosed. Because the addition is done in little amounts the quadratic terms of the concentration can be neglected and the relation (5) becomes:

$$I_x = k c_x. \quad (6)$$

For the sample obtained through the growth of concentration:

$$I'_x = k (c_x + \Delta c), \quad (7)$$

then we immediately obtain:

$$c_x = \Delta c \frac{I_x}{I'_x - I_x}. \quad (8)$$

Through successive additions of little known amounts from same elements there is obtained an array of sample practically with a constant matrix. The measurements of the fluorescence radiation intensity permit the determination of the calibration line. The extrapolation of the calibration line up to level r_x permits the determination of the concentration for the element that must be dosed (see figure 2). To draw the calibration line we can use the least-squares method.

The dilution method is based on the same principle used in the frame of the addition method. The difference consists in the introduction of an inert diluent (lithium tetraborate) to the RX fluorescence radiation. The sample is obtained through mixing of the Li or Na tetraborate with the analyzed sample followed by the vitrification through thermic treatment. Through the diluent addition the investigated element concentration decrease with ΔC , amount that can be calculated with relation:

$$C_x = \Delta C \frac{I_x}{I_x - I_x'} \quad (9)$$

The multiple dilution method is similar to the multiple addition method, the dosed element concentration being determined through the extrapolation of calibration line to the point determined by the count rate of the detector for unknown concentration.

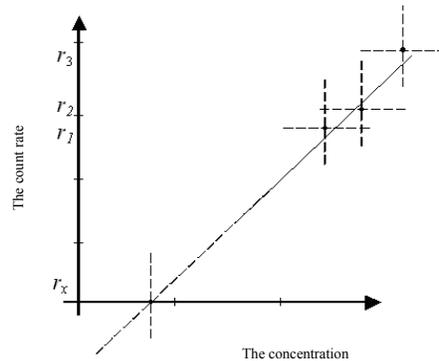


Fig. 2. The determination of concentration for the element that must be dosed

The Sample Preparation

The technical problem in this case is represented by finishing the samples surfaces that must have fine roughness. The X-ray fluorescence X using the characteristic X radiation energy, even for the heavy elements, doesn't exceed 100KeV and this is practically analysis method confined to the superficial zones of the samples. Thereby, for the fluorescence radiation of iron the depth of saturation is about 20μ , the radiation produced at greater a depth can't be outward to the sample, in order to be detected. This method refers to superficial analysis, the accuracy and the repeatability of the results shall be strongly affected by the surface smoothness.

Experimentally there was observed a diminution of the fluorescence radiation intensity with the growth of the sizes of the granules from the sample. At the same time, for the samples having a nonhomogeneous granular structure, the experimental results concerning the dosage of different elements, through X-ray fluorescence, presents important fluctuations even for different zones belonging to the same samples.

Given this reason the surface preparation method of the samples, play a crucial role in obtaining the above graded measurements. The methods currently used for the preparation of the samples have as aim also to reduce, as much as possible, the influence of the granulation and inhomogeneities of these surfaces.

The easiest method of preparation consists in a fine polishing of the samples surfaces so that the roughness to doesn't exceed $5-10\mu$. This method is used for metallic and geological samples.

In the situation in which, from different causes, the investigated samples are in pulverulent state, is recommended to riddle them to select the granulometric fraction having the size less than 10μ , thereto the selected fraction is mixed with an inert binding matter (styrene or methyl methacrylate) up to the complete homogenization. After that, the prepared samples are maintained at high temperature for polymerization of the binding matter, these are compressed using a hydraulic press. Finally, using this method of preparation, we obtain extremely

homogeneous samples whose surface is sufficiently smooth in order not to influence, in a negative way, the determination accuracy.

The most proper way to produce high quality samples consists in their vitrification. According to this procedure, the materials that must be investigated are crushed, mixed with a certain amount of lithium tetraborate, thereto the obtained mixture is warmed up to a temperature where all components merge, resulting a perfect homogeneous glass piece. After cooling, the surface of the obtained sample is finely polished, thereto used to execute measurements. This preparation method presents a supplementary advantage, namely it reduces the matrix effects as a consequence of supplement dilution of a samples using lithium tetraborate.

The effects connected to the samples inhomogeneities or to the surface rugosities disappear completely in the case of the liquid samples, but this not always possible.

Isotopic Sources for Excitation

For the excitation of the fluorescent radiation emission, there can be used an innumerability of isotopic or instrumental sources. Good results were reported the use of the isotopic sources of radiations α , β or soft γ . Nevertheless the most proper excitation sources for this type of measurements consist in an X-rays tube given its high intensity emissive radiation. Because, the X-ray fluorescence is a method of surface analysis, it is obvious that the sources of used radiations shall be due to a proper geometry, in the sense that the surface must present large dimensions, preferably the same order of size with the sample's surface. From this are used isotopic sources with discoid forms or ring-shaped or X-ray tubes with flat anode.

- The radiations sources are used for the excitation of the fluorescent radiation for easy elements having the atomic number less then 12 but, due to a marked diminishing of the fluorescence efficaciousness with the atomic number, practically these are used for elements contained between oxygen ($Z = 8$) and chlorine ($Z = 19$). Also, the strong attenuation of the radiation in air involves the utilization vacuous space for irradiation, which creates certain difficulties in the realization of the measuring installation.
- The β radiation sources are used successfully for the fluorescent radiation excitation of the elements having the atomic numbers superior to the argon atomic number, the elements for which the efficaciousness of fluorescence is sensitively greater than zero. The excitation through the irradiation with radiations is done both through direct interaction of electrons and through braking X-ray of generated_of these as much in sample how much in the source support. Also in the category of the isotopic sources of β radiations, there can be included the several active β^+ sources for which the electronic capture is around 10%, the characteristic X-ray being the effective source of excitation. The excitation of the fluorescent radiation is achieved with higher efficaciousness of to the β radiation than the excitation by the bremsstrahlung radiation that appears in the support of the source.
- The sources of X-rays and soft γ rays are used for the excitation of the fluorescent radiation of average-Z elements and high-Z elements. Because the majority of these sources are are β -active, the energetic spectrum of the emitted radiations shall consist in overlapping bremsstrahlungs, characteristic X-rays and soft γ rays.

In table 1 there are presented the features of some important isotopic sources used for the excitation of the fluorescent X-rays and in table 2 there are presented the characteristics of some analyzer crystals.

A remarkable growth efficaciousness of excitation using bremsstrahlung is obtained if element on which is deposited the β source, selected in way that the bremsstrahlung energy exceed

merely with little the limit of absorption peak for the heaviest elements that must be dosed from the investigated sample. This thing leads to a favorable report between the intensity of the characteristic X-ray emitted by the sample and the intensity of the scattered X-rays by the sample through Compton Effect.

At the same time there must be taken into account the diminution number of order of the investigated elements can't be extended down to first elements from the periodic table (He, Li, Be), for which the emission of the photons of fluorescence diminishes sensitively, given favor to the emission of the electrons Auger.

Table 1. Isotopic sources used for the excitation of the fluorescent X-rays.

Radionuclide	Half-life	Decay mode	Emitted radiation energy (keV)	Elements that can be analyzed
Po-210	128 d	α	530	C, Cl (K_{α})
Pu-238	86,4 y	α, γ	12-17(U, L_{α})	Nd, U (L_{α})
Am-241	458 y	α, γ	14-21 (Np, L_{α}) 6, 26, 59 (γ moi)	Nd, U (L_{α}) Ca, Tm (K_{α})
Fe-55	2.7y	CE	5,9 (Mn, K_{α})	P, V (K_{α})
Cd-109	470 d	CE, γ	22 (Ag, K_{α}) 88 (γ moi)	Fe, Ru (K_{α})
Gd-153	236 d	CE, γ	42 (Eu, K_{α}) 97, 103 (γ moi)	Mo, Ra (K_{α})
Co-153	270 d	CE, γ	6.4 (Fe, K_{α}) 14, 122, 139 (γ moi)	Ag, Cf (K_{α})
H-3/Zr	12,2 y	β	5-12 (bremsstrahlungs) 18 (Zr, K_{α})	Ag, Tm (L_{α}) Cr, Zn (K_{α}) Fe, Si (K_{α})
Pm-147/Al Pm-147/Zr	2,6 y	β	10-100 18 (Zr, K_{α})	Fe, Tm (K_{α}) Tm, U (L_{α})
I-125	60 d	CE, γ	27,7 (Te, K_{α}) 35 (γ moi)	Ca, Te (K_{α})

Table 2. Characteristics of some analyzer crystals

The Cristal	2d (nm)	Diffraction plane	Measuring domain	Practically used domain
LiF	0,402	(200)	> K	Ti-U
Ge	0,6532	(111)	> P	P-Ca
PET (penta erithral)	0,876	(002)	> Al	Al-Si
BFT (bifalat de Ta)	2,590	(001)	> O	O-Mg

Based on datasets from the technical literature, figure 3 represents the dependency of square roots from the excitation energy of the emitted radiation depending on the atomic number for different elements from the Mendeleev periodic table. As already noticed this dependency can be considered, in a good approximation as linear.

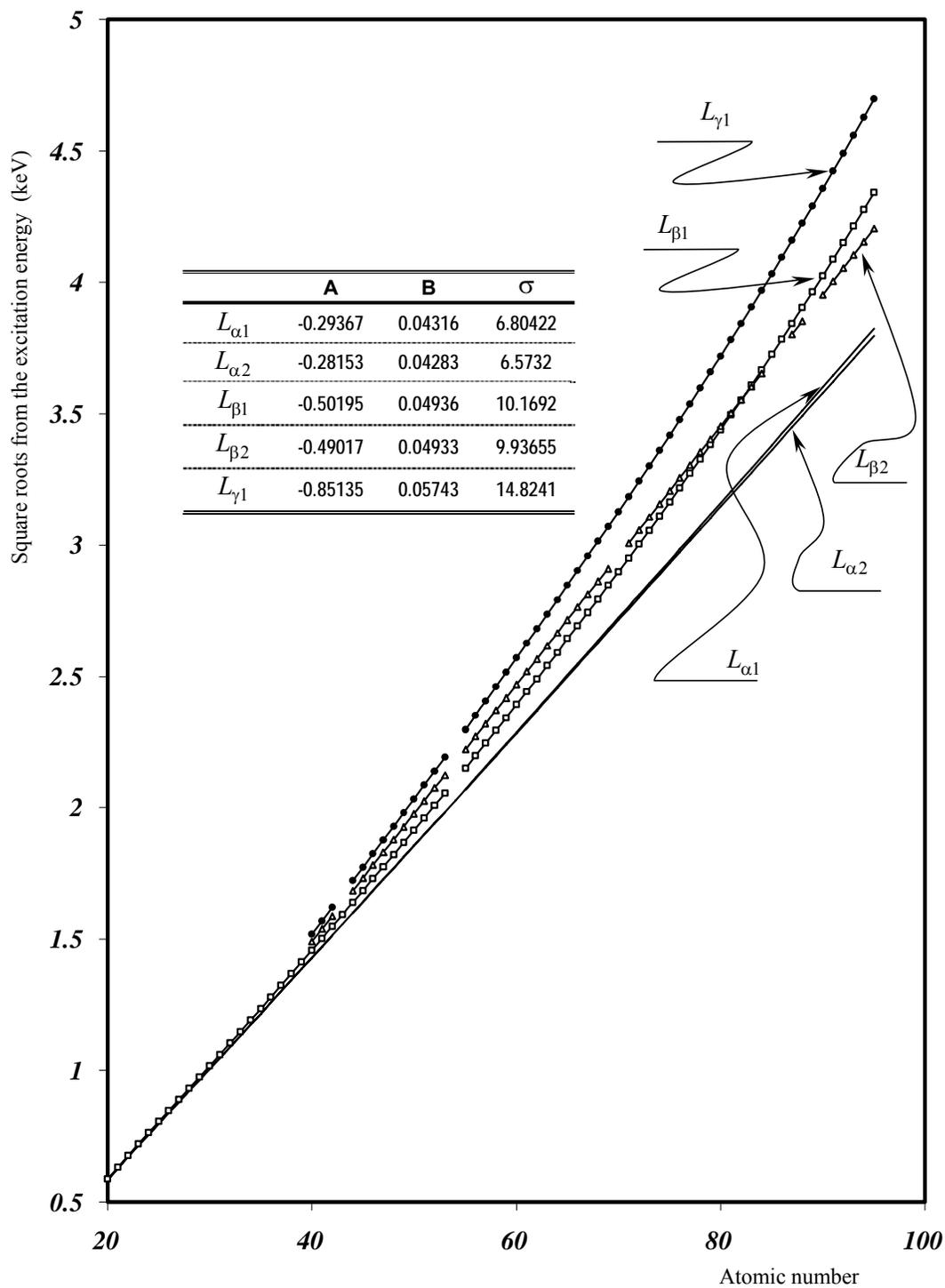


Fig. 3. Square roots from the excitation energy relative to the atomic number

Conclusion

The method of the X-ray fluorescence, used for concentration determination of an element in a sample, is very precise. The work presents, in fact, one of the procedures that allows for the determination concentration of an element using the method of the X-ray fluorescence. Taking into consideration that the Moseley law is precisely on relative limited areas of atomic numbers, the diversification of the practical procedures based on the method of the X-ray fluorescence is strictly necessary.

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Fluorescența de radiații X

Rezumat

Fluorescența de radiații X este o metodă nedistructivă folosită pentru determinarea calitativă și cantitativă a compoziției chimice elementare a unor probe cu număr diferit de elemente. Avantajul principal al analizei radiației de fluorescență din domeniul radiațiilor X constă în simplitatea spectrului acestora. Vacantarea diferitelor niveluri electronice profunde ale atomilor este urmată de apariția fenomenului de fluorescență de radiații X. Acest fenomen nu este dependent de mecanismul prin care sunt create vacanțele electronice în păturile profunde ale atomilor fiind dependent de numărul atomic Z al elementului. Această metodă poate fi folosită fără restricții la dozarea tuturor elementelor din tabelul periodic cu $Z > 12$.