ISSN 1027-5495. Functional Materials, 27, No.3 (2020), p. 628-637.
doi:https://doi.org/10.15407/fm27.03.628

X-ray analysis of materials by the ratio of the intensities of incoherent and coherent scattering

A.I.Mikhailov

Department of Physics of Metals and Semiconductors, National Technical University "Kharkiv Polytechnic Institute", 2 Kyrpychova Str., 61002 Kharkiv, Ukraine

Received April 15, 2020

The fundamental possibility of quick identification of materials by the ratio of the intensities of incoherent and coherent scattering I_C/I_R is shown. Unlike traditional X-ray fluorescence analysis, identification is possible in the absence of a relationship between the positions of the scattering peaks and the composition of the sample, and a qualitative and quantitative analyses of the composition of the material is carried out in the framework of solving one inverse problem. The method is based on the dependence of the I_C/I_R ratio on the effective atomic number of the scatterer material and the spectrum registration conditions (momentum transfer variable $x = \sin\theta/\lambda$). The experiments were carried out for one-component materials with atomic number Z from 4 (Be) to 31 (Ga) and binary compounds with stoichiometric composition at two values of $x_1 = 0.831$ Å^{-1} and $x_2 = 1.297$ Å^{-1} using a WDXRF spectrometer. The set of calibration functions $I_C/I_R(Z, x)$ allows to create a system of linear equations whose solutions are the concentrations and atomic numbers of the chemical elements that make up the material. The high photon energy of scattered radiation (17.44 keV) makes it possible to detect light impurities, starting from hydrogen ($Z = 1$), and the smaller the atomic number of the impurity, the higher the sensitivity of the method.

Keywords: Compton-to-Rayleigh scattering intensity ratio, effective atomic number, light elements.

Рентгенівський аналіз матеріалів за співвідношенням інтенсивності некогерентного і когерентного розсіювання. *А.І.Михайлов*

Показано принципову можливість швидкої ідентифікації матеріалів за співвідношенням інтенсивності некогерентного і когерентного розсіювання I_C/I_R. На відміну від традиційного рентгенофлуоресцентного аналізу ідентифікація можлива за відсутності взаємозв'язку між положеннями піків розсіювання і складом зразка, а якісний і кількісний аналіз складу матеріалу проводяться у рамках вирішення однієї оберненої задачі. Метод заснований на залежності співвідношення I_C/I_R від ефективного атомного номера матеріалу розсіювача і умов реєстрації спектра (змінна перенесення імпульсу $x = \sin\theta/\lambda$). Експерименти проведено для однокомпонентних матеріалів з атомним номером Z від 4 (Be) до 31 (Ga) і бінарних сполук стехіометричного складу при двох значеннях $x_1 = 0.831$ Å^{-1} та $x_2 = 1.297$ Å^{-1} за допомогою спектрометра WDXRF. Набір калібрувальних функцій $I_C/I_R(Z, x)$ дозволяє скласти систему лінійних рівнянь, рішеннями якої є концентрації і атомні номери хімічних елементів, що входять до складу матеріалу. Висока енергія фотонів розсіяного випромінювання (17,44 кеВ) дозволяє виявляти легкі домішки, починаючи від водню ($Z = 1$), причому чим менше атомний номер домішки, тим вище чутливість методу.

Показана принципиальная возможность быстрой идентификации материалов по соотношению интенсивностей некогерентного и когерентного рассеяний I_C/I_R. В отличие от традиционного рентгенофлуоресцентного анализа идентификация возможна при отсутствии взаимосвязи между положениями пиков рассеяния и составом образца, а качественный и количественный анализ состава материала проводится в рамках решения одной обратной задачи. Метод основан на зависимости соотношения I_C/I_R от эффективного атомного номера материала рассеивателя и условий регистрации спектра (переменная переноса импульса $x = \sin\theta/\lambda$). Эксперименты проведены для однокомпонентных материалов с атомным номером Z от 4 (Be) до 31 (Ga) и бинарных соединений стехиометрического состава при двух значениях $x_1 = 0.831$ Å^{-1} и $x_2 = 1.297$ Å^{-1} с помощью спектрометра WDXRF. Набор калибровочных функций $I_C/I_R(Z, x)$ позволяет составить систему линейных уравнений, решениями которой являются концентрации и атомные номера химических элементов входящих в состав материала. Высокая энергия фотонов рассеянного излучения (17,44 кэВ) позволяет выявлять легкие примеси, начиная от водорода ($Z = 1$), причем чем меньше атомный номер примеси, тем выше чувствительность метода.

1. Introduction

The traditional X-ray method for determining the chemical composition of materials is based on the Mosley law [1], which relates the wavelength of the fluorescent radiation of an element to its atomic number. According to this law, with a decrease in the atomic number, the wavelength of the characteristic radiation of the chemical element increases; this imposes significant restrictions: chemical elements with a small atomic number remain inaccessible to X-ray methods. This is due to a sharp decrease in the fluorescence yield and low penetrating ability of X-rays with an energy $E < 1$ keV. The low photon energy of the secondary radiation causes an extremely shallow depth of the information layer (100 Å). Therefore, the reliability of the results of intensity measurements is significantly affected by granulometry and the surface topography of the sample. The fluorescence emission of chemical elements with atomic number $Z < 9$ gets into the energy range $E < 1$ keV. Research in this range is an urgent task for many branches of science and technology, namely: the combination of elements H, C, O, N is the basis of wildlife; H, C and O elements form the basis of fuel, and Be and B are part of promising structural materials.

Obviously, to solve such analytical problems, it is necessary that the energy of the analytical signal be as large as possible. This possibility is provided by the use of primary radiation with an energy of more than 10 keV scattered on the analyzed sample.

In the classic work of Compton [2], a method is described that, in principle, allows one to determine the atomic number of a chemical element from the ratio of the integrated intensities of incoherent (Compton) and coherent (Rayleigh) scattering $I_C/I_R(Z)$. The uniqueness of this method lies in the fact that it is suitable for quick identification of elements with a small atomic number starting from hydrogen ($Z = 1$), for example, according to the Tables [3], and the smaller the atomic number, the higher the sensitivity of the method. In the very first experimental works [4, 5], a complex form of the dependence $I_C/I_R(Z)$ was established. In [5], direct experiments on X-ray scattering on gases with atomic numbers from $Z = 7$ (N) to $Z = 10$ (Ar) revealed the presence of a "plateau" for which the derivative of the function $I_C/I_R(Z)$ is close to zero. In this Z range, it is impossible to use the function $I_C/I_R(Z)$ as a calibration function for identifying elements.

Over the past thirty years, many experimental studies have been carried out to measure the absolute magnitude of the intensity of each of the scattering peaks. It was shown in [6, 7] that such measurements are very complex experimentally and require a number of corrections taking into account the geometry of the measuring circuit and absorption both in the scatterer material and in the detector window, detector efficiency, etc. The corrections are very significant and substantially affect the accuracy of the measurement results. In order to avoid the use of the corrections, the absolute measurements of the scattering peaks were replaced by measuring the ratio of their integrated intensities. In this case, the correction of the experimental data is reduced to taking into account the difference in the absorption coefficients of Compton and Rayleigh scattered photons, which are very close in energy.

Traditional measurements of the intensities of these peaks were used to solve the

fundamental problems of determining the effective atomic number and mass absorption coefficients [8, 9]. Measuring the intensity of scattering peaks is widely used in various fields to solve applied problems: composition selection in XRF analysis [10], in pharmaceuticals [11], in the coal industry [12] for studying coatings [13]. However, the method was not used directly for the quantitative and quantitative analyses of multicomponent materials. This is due to the fact that the calibration function $I_C/I_R(Z)$ allows to determine one value of the atomic number at 100 % concentration, and multicomponent materials consist of several chemical elements with different atomic numbers and different concentrations.

For the first time to identify multicomponent materials, it is proposed to use the dependence of the intensity of the scattered radiation on the conditions of spectrum registration, namely, on the momentum transfer variable $x = (\sin\theta/\lambda)$, where θ is the scattering angle and λ is the wavelength of the scattered radiation. The set of calibration functions $I_C/I_R(Z, x)$ allows you to create a system of linear equations, the solutions of which are the concentration and atomic numbers of the chemical elements that make up the material. It is fundamentally important that this identification is possible in the absence of a relationship between the positions of the scattering peaks and the composition of the sample, and a qualitative and quantitative analyses of the composition of the material is carried out in the framework of solving one inverse problem.

The purpose of the work is to show the fundamental possibility of studying the composition of multicomponent materials by the ratio of the intensities of incoherent and coherent X-ray scattering.

2. Theory

According to the Pirenne review [14], the total intensity of the unpolarized primary radiation scattered by an isolated atom is determined by the formula:

$$I_S = I_0 \frac{a_e^2}{R^2} \frac{1 + \cos^2 2\theta}{2} [f^2 + QZS], \quad (1)$$

$$\text{where } Q = \left(1 + \frac{h(1 - \cos 2\theta)}{m_e c \lambda}\right)^{-3}$$

where Q is the relativistic correction for incoherent radiation; h is Planck's constant; m_e is the rest mass of the electron; c is the speed of light; λ is the wavelength of the scattered radiation (in Å); I_0 is the intensity of the primary beam; a_e is the classical radius of an electron; R is the distance from the sample; 2θ is the scattering angle, f is the atomic scattering factor for X-ray radiation, Z is the atomic number, S is the Heisenberg-Bevilogua incoherent scattering function [15].

In equation (1), the expression in parentheses defines the components of coherent $f(x)$ and incoherent $S(x)$ scattering. Assuming the additive contribution of individual atoms to coherent and incoherent X-ray scattering [16, 17] for a scatterer containing chemical elements with atomic numbers Z_i in atomic fractions C_i, we obtain the following expression

$$\frac{I_C}{I_R} = \frac{[\frac{\partial\sigma}{\partial\Omega}]_{KN} \sum C_i Z_i S(x, Z_i)}{[\frac{\partial\sigma}{\partial\Omega}]_T \sum C_i f^2(x, Z_i)} P(\varphi,\psi), \quad (2)$$

where

$$P(\varphi,\psi) = (1+\frac{\sin\varphi\,\mu_C}{\sin\psi\,\mu_R}) / (1+\frac{\sin\varphi}{\sin\psi}) P_W P_{air}$$

is a factor that takes into account the difference between the absorption coefficients μ_R and μ_C for photons of coherent and incoherent scattering in the material of the scatterer. P_W and P_{air} are coefficients that take into account different absorption in the detector window and in the air gap of the spectrometer; φ and ψ are the angles of incidence and emission of radiation, respectively, $\left[\frac{\partial\sigma}{\partial\Omega}\right]_{KN}$ and $\left[\frac{\partial\sigma}{\partial\Omega}\right]_T$ are, respectively , differential Klein-Nishina and Thomson cross sections for electron scattering.

The coefficients P_W and P_{air} are determined by the geometry of the spectrometer, and the ratio μ_C/μ_R is independent of the composition of the sample. Indeed, if in the range between the photon energies of coherent and incoherent scattering there are no absorption jumps for chemical elements of the scattering material, the value of μ is proportional to $\lambda^{2.7-2.9}$ for any chemical element. Then the ratio is determined by the difference, and hence the scattering angle 2θ:

$$\Delta\lambda = 0.02426\,(1 - \cos 2\theta), \text{ [Å]}. \quad (3)$$

Accordingly, the value of $P(\varphi, \psi)$ is constant under given measurement conditions and can be calculated in advance. At the photon energy of the primary radiation (E =

17.4 keV), the relative difference between the energies of coherent and incoherent scattering does not exceed several percent; therefore, the ratio of the differential Klein-Nishina and Thomson cross sections for electron scattering can be considered equal to unity.

The proposed method is based on determining the effective atomic number from the observed scattering property. Several definitions of the effective atomic number $Z_{eff}(x)$ are known for multicomponent materials [16]. Some of them depend only on the ratio of the atomic weights of the components in the compound and are not related to the measured scattering property. In accordance with [16] and using equation (2), we introduce the definition of the effective atomic number of the scatterer. The effective atomic number $Z_{eff}(x)$ is determined from the condition that the one-component material has an interpolated atomic number $Z_{eff}(x)$, for which equation (2) gives the same I_C/I_R ratio as for the multicomponent test compound:

$$\frac{I_C}{I_R} = \frac{Z_{eff}S(x,Z_{eff})}{f^2(x,Z_{eff})}P(\varphi,\psi) \qquad (4)$$

or

$$Z_{eff} = \frac{f^2(x,Z_{eff})\sum C_i Z_i S(x,Z_i)}{S(x,Z_{eff})\ \sum C_i f_i^2(x,Z_i)}. \qquad (5)$$

From this definition it follows that for a single-component material, the value $Z_{eff}(x)$ is independent on x and is equal to the atomic number Z. For a multicomponent substance, the value of $Z_{eff}(x)$ always depends on x, and this dependence increases with the difference in atomic numbers of the components of the scatterer. By changing the conditions for registering the spectrum, for example, by using primary radiation with different wavelengths, we can obtain a set of calibration functions $I_C/I_R(Z, x)$. This will make it possible to compose a system of linear equations, which has a unique solution if its determinant is not equal to zero.

For example, consider a binary compound. Let the values of $g(x, C_1, C_2, Z_1, Z_2)$ correspond to the ratio of experimentally measured intensities $I_C I_R$. For scattered radiation with photon energy $E = 17.4$ keV, equation (2) can be written as:

$$\sum C_i\{g(x,C_1,C_2,Z_1,Z_2)f^2(x,Z_i) - Z_i S(x,Z_i)P(\varphi,\psi)\} = 0, \qquad (6)$$

where $S(x, Z_i)$ and $f^2(x, Z_i)$ are table values. Then:

$$\sum C_i f^2(x,Z_i)\Big(g(x,C_1,C_2,Z_1,Z_2) - y(x,Z_i)\Big) = 0. \qquad (7)$$

Here the function $y(x,Z_i)=\frac{Z_i S(x,Z_i)}{f_i^2(x,Z_i)}P(\varphi,\psi)$ can be theoretically calculated for any chemical element, for example, according to the Hubbell tables [3]. However, it should be noted that in the Hubbell tables the values $S(x, Z)$ correspond to $ZS(x, Z)$ in the Heisenberg notation. Equation (7) together with the normalization condition $\sum C_i = 1$ will compose a system of linear equations for atomic concentrations of elements of a binary compound with coefficients for unknowns:

$$f^2(x,Z_i)(g(x,C_1,C_2,\ldots,Z_1,Z_2,\ldots) - y(x,Z_i)) = 0.$$

The main difficulty of the method is that the wavelength of the scattered radiation does not depend on the atomic number of the scatterer. Accordingly, the positions of the peaks in the scattering spectrum cannot be used to determine the atomic number, in contrast to the X-ray fluorescence analysis based on the Mosley law. Therefore, the atomic numbers Z_i of all components and their concentrations in a multicomponent material are identified by the ratio measured at various x values. Thus, qualitative and quantitative analyses are inseparable in the scattering method.

3. Objects of study and X-ray techniques

The objects of the study were:

1) one-component samples with a purity of at least 99.5 wt.% mass: Be ($Z = 4$), B ($Z = 5$), C ($Z = 6$), Mg ($Z = 12$), Al ($Z = 13$), Si ($Z = 14$), S ($Z = 16$), Ti ($Z = 22$), V ($Z = 23$), Cr ($Z = 24$), Mn ($Z = 25$), Fe ($Z = 26$), Co ($Z = 27$), Ni ($Z = 28$), Cu ($Z = 29$), Zn ($Z = 30$) and Ga ($Z = 31$);

2) compounds of a stoichiometric composition with an impurity content of not more than 0.5 wt.%: B_4C, LiF, MgO, Al_2O_3, SiO_2, CaF_2, NaCl, Fe_2O_3, KCl, GaP, GaAs, C_2H_6O, H_2O, Li_2CO_3, $Li_2B_4O_7$ and B_2O_3.

3) mixtures of chemically pure compounds Al + $Al(OH)_3$ with a mass fraction of aluminum from 35 to 68 wt.%.

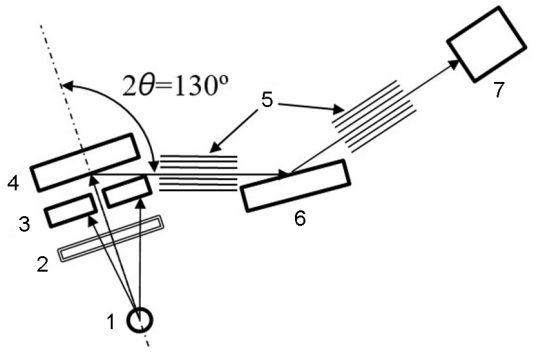

Fig. 1. Schematic of measurements of scattered radiation in a WDXRF spectrometer: *1* — radiation source; *2* — place for the installation of a secondary target from selenium; *3* — curtain (diaphragm); *4* — sample; *5* — Soller collimators; *6* — crystal analyzer LiF (002); *7* — scintillation detector.

The materials were prepared at the NSC KIPT (National Science Center Kharkiv Institute of Physics and Technology, Kharkiv, Ukraine), the Institute of Single Crystals (Kharkov, Ukraine), the Plant of Pure Metals (Svetlovodsk, Ukraine), the Institute of Metallurgy and Materials Science named after M.A. Baykov (Moscow, Russia), State Research and Design Institute of the rare-metal industry of OJSC "Giredmet" (Moscow, Russia). Standard samples of Al + $Al(OH)_3$ powder mixtures were prepared in the laboratory of PJSC Mariupol Ilyich Metallurgical Plant (Mariupol, Ukraine).

The spectra were measured on a SPRUT SEF 01 K scanning crystal diffraction spectrometer according to the reflection scheme shown in Fig. 1. The choice of the X-ray optical scheme is explained by the best energy resolution; at this, the high photon energy of the detected radiation allows the detector to be sufficiently distanced.

The measurements were carried out in two radiations: Mo–Kα λ = 0.71 Å and Se–Kα λ = 1.106 Å. In the first case, the characteristic radiation of the anode of the X-ray tube was used. In the second, a secondary target from selenium was installed additionally (Fig. 1, pos. 2). Scattering spectra were recorded by scanning with a step width Δλ = 0.002 Å and an exposure of 10 s at each measurement point. The profile shape of the scattered peak was approximated by the Pearson functions VII, $I(t) = I_0/(1 + kt^2)^m$, where $k = (2^{(1/m)} - 1)/(\omega/2)$ $I(t)$; ω is the peak width at half maximum; m is the shape factor.

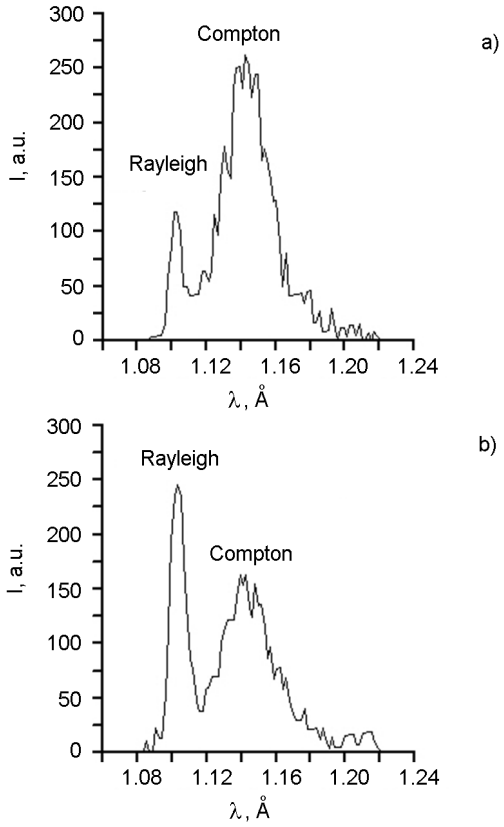

Fig. 2. a) A fragment of the Be (Z = 4) scattering spectrum obtained with primary radiation of Se–Kα (λ = 1.106 Å) and sinθ/λ = 0.831 Å; b) A fragment of the C (Z = 6) scattering spectrum obtained with primary radiation of Se–Kα (λ = 1.106 Å) and sinθ/λ = 0.831 Å.

The scattering angle 2θ was determined for each sample by the formula (3). The value of this angle was 2θ = 130±2°. The correction for absorption, $P(\varphi, \psi)$, was 0.901 for Mo–Kα and 0.938 for Se–Kα. The error of the experimental values did not exceed ±2 %.

4. Results and discussion

4.1.Calibration function

Fig. 2a and 2b show the experimental scattering spectra of Be (Z = 4) and C (Z = 6). The ratio of the intensities of Compton and Rayleigh peaks is significant even for materials with close atomic numbers, which ensures high sensitivity in determining the effective atomic number.

Fig. 3 shows the experimental dependence of the ratio of scattering peaks on the atomic number of the scatterer. It is very important that the ratios of the integrated

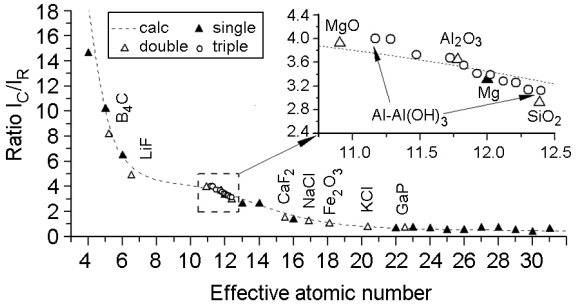

Fig. 3. The ratio of the scattering peaks vs the atomic number of the scatterer, obtained by the WDXRF method.

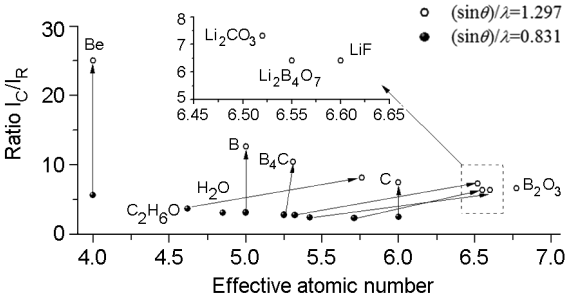

Fig. 4. Experimental dependences of the I_C/I_R ratio on the effective atomic number of the scatterer at two different values: x_1 = 0.831 Å^{-1} and x_2 = 1.297 Å^{-1}.

intensities that were experimentally measured for one-component standards and multicomponent materials with a stoichiometric composition lie on the same curve. This means that the obtained curve can be used as a calibration curve for determining the composition of an unknown two-component sample. All the spectra were obtained using standard samples; therefore, the given dependences $Z_{eff}(x)$ are calibration curves.

The most interesting is the complex form of the relationship I_C/I_R in the range from $Z = 4$ to $Z = 18$. The curve drops sharply in the range from $Z = 4$ to $Z = 7$; then, in the Z range from 8 to 10, a "plateau" is observed, which was experimentally discovered in earlier works [4] and [5]. In the range from $Z = 10$ to $Z = 16$, the curve drops sharply again, and when $Z > 18$, it reaches an asymptotic value.

For practical measurements, the most important are the sections of the curve where the derivative is significantly different from zero. We carefully studied the range from $Z = 10$ to $Z = 16$ by measuring binary stoichiometric composition systems and three-component standard mixtures Al + Al(OH)$_3$. For three-component mixtures, the dependence I_C/I_R is very close to that obtained for two-component samples, although it has a sharper slope (insert in Fig. 3). Detailed measurements also allowed us to clarify the position of the right edge of the plateau and the beginning of the decline near $Z = 11$. To estimate the measurement error, when the atomic number of the scatterer is determined by the calibration graph, we use the formula:

$$\Delta Z_{eff} = \Delta g(Z_{eff}) / \frac{\partial g(Z_{eff})}{\partial Z_{eff}} ,$$

where $\Delta g(Z_{eff})$ is the experimental error in measuring the ratio of intensities of scattering peaks. In the Z range from 4 to 7, the derivative reaches 3.7 per atomic number and $\Delta g(Z_{eff}) = \pm 0.5$. Therefore, the effective atomic number is determined with a low error $\Delta Z_{eff} = \pm 0.14$. Similarly, for the Z range from 11 to 18, we have the derivative value of 0.43 and $\Delta g(Z_{eff}) = \pm 0.3$; then $\Delta Z_{eff} = \pm 0.69$.

Thus, the calibration curve can be used to determine the effective atomic number of the scatterer in the two indicated Z ranges with high accuracy.

4.2. Material identification

Fig. 4 illustrates the dependence of $Z_{eff}(x)$ on the measurement conditions $x = (\sin\theta/\lambda)$. The calibration functions constructed from the experimental data measured at different values of x differ not only in the ordinate and slope (derivative), but also in the position of the same points along the abscissa (indicated by arrows).

Small deviations (an enlarged fragment) of the experimental values from the theoretical dependences $S(x, Z_i)$ and $f^2(x, Z_i)$ are observed [3, 18]. Therefore, to reduce the influence of noise of a single measurement in the calculations, we used the regularization solution [1] of the experimental calibration function by $Z_{eff}(x)$.

The regularization solutions for these curves are given by the equations: for $x_1 = 0.831$, $y_1 = -0.151 \cdot Z^3 + 3.308 \cdot Z^2 - 23.20 \cdot Z + 55.13$, the error is 3.2 %; for $x_2 = 1.297$, $y_2 = 0.393 \cdot Z^3 + 9.342 \cdot Z^2 - 72.33 \cdot Z + 190.0$, the error is 1.08 %. Based on these solutions, the values of $y(x, Z_i)$ were calculated for a one-component scatterer with atomic number Z_i (Table 1).

Unfortunately, this calibration is difficult to construct in a wide range of $Z_{eff}(x)$ due to the impossibility of preparing stand-

Table 1. Calculated of $Z_{eff}(x)$ for different scatterer materials at different x_1 = 0.831 Å^{-1} and x_2 = Å^{-1}. The values of $g(x)$ and $y(x, Z)$ are, respectively, the experimentally measured and theoretically calculated ratios of the intensities of coherent and incoherent scattering, I_C/I_R

Sample	x_1 = 0.831 Å^{-1}			x_2 = 1.297 Å^{-1}		
	Z_{eff1}	$g(x_1)$	y_1	Z_{eff2}	$g(x_2)$	y_2
Li	3	–	10.0	3	–	108
Be	4	5.64	5.63	4	25	25.0
C_2H_6O	4.62	3.68	3.70	5.76	10.2	8.17
H_2O	4.85	3.09	3.23	6.54	–	–
B	5	3.13	3.00	5	12.7	12.74
B_4C	5.25	2.80	2.70	5.31	10.48	10.46
Li_2CO_3	5.32	2.75	2.64	6.52	7.3	6.54
LiF	5.42	2.44	2.57	6.60	6.4	6.50
$Li_2B_4O_7$	5.71	2.34	2.44	6.55	6.4	6.52
C	6	2.51	2.45	6	7.5	7.39
N	7	–	2.2	7	–	5.94
O	8	–	2.1	8	–	5.08
F	9	–	2.0	9	–	4.7

ard samples suitable for measurements. However, if the experimental calibration is in good agreement with the theoretical dependence, interpolation outside the calibration range $Z_{eff}(x) = 4–6.8$ can be applied up to $Z = 9$ (F). It is difficult to justify the interpolation of the calibration according to the theoretical dependence using the Tables [3] for $Z_{eff}(x)\leq 3$ due to the lack of experimental points. Nevertheless, this interpolation allows a qualitative assessment of the scatterer material containing lithium and hydrogen.

Consider an algorithm for determining a two-component substance. Let the experimental measurements of the ratio I_C/I_R give the values $g(x_1)$ and $g(x_2)$ for x_1 and x_2. The corresponding Z_{eff1} and Z_{eff2} values are found using two calibrations for these values. For a two-component compound, it is convenient to divide system (5) into two systems of equations, taking into account the normalization:

$$\begin{cases} C_1(g(x_1) - y_1(Z_1)) + C_2(g(x_1) - y_1(Z_2)) = 0 \\ C_1 + C_2 = 1, \end{cases} \quad (8)$$

$$\begin{cases} C_1'(g(x_2) - y_2(Z_1)) + C_2'(g(x_2) - y_2(Z_2)) = 0 \\ C_1' + C_2' = 1. \end{cases} \quad (9)$$

These are systems of linear equations for concentrations C_1 and C_1'. Each of them has a unique solution for given values of Z_1 and Z_2. The criterion for the correct determination of a binary substance is the coincidence of the solutions of equations (8) and (9) for these values of Z_1 and Z_2 within the measurement error.

Table 2. Atomic concentrations of the first chemical elements included in the binary systems obtained from the approximation of parameters C_1 and C_1' using equations (8) and (9)

Combination of elements	C_1	C_1'
B–N	0.407	0.017
B–O	0.534	0.414
B–F	0.644	0.519
Be–N	0.171	0.128
Be–O	0.255	0.351
Be–F	0.351	0.452
Li–N	0.200	0.128
Li–O	0.293	0.350
Li–F	0.43	0.451

Let's look at two examples.

Example 1: $g(x_1) = 2.80$, $g(x_2) = 10.48$

According to calibration graphs, $Z_{eff1} \approx Z_{eff2} \approx 5.3$. For fitting, choose boron ($Z = 5$) and carbon ($Z = 6$). Using Table 1 we have for boron $y_1(5) = 3.00$ $y_2(5) = 12.7$ and for carbon $y_1(6) = 2.45$, $y_2(6) = 7.39$. Solutions of systems (6): $C_B = 0.72$ and (7): $C_B = 0.71$ are similar.

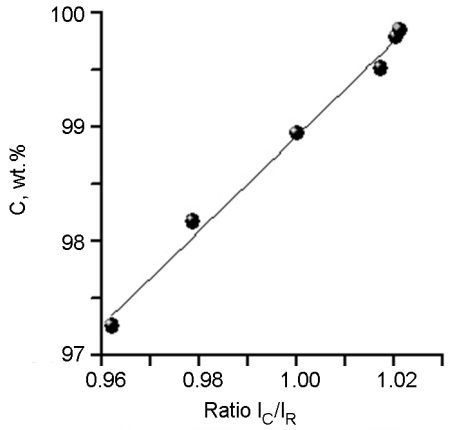

Fig. 5. Calibration function for standard samples of primary aluminum.

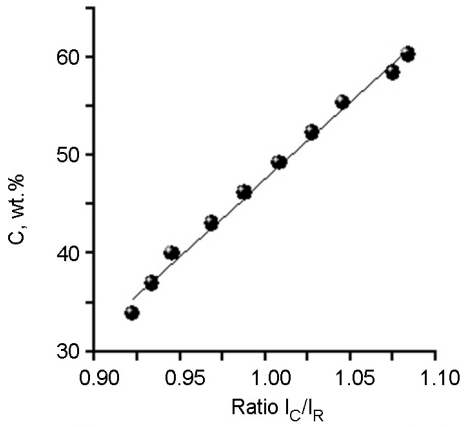

Fig. 6. Calibration function for $Al–Al_2O_3$ powder mixtures according to oxygen content.

Thus, a binary compound of boron and carbon with a boron concentration of 0.72 was identified, which is close to the real value of 0.8 for sample B_4C.

Example 2: $g(x_1) = 2.44$, $g(x_2) = 6.40$.

According to calibration graphs: $Z_{eff1} \approx 5.4$, $Z_{eff2} \approx 6.6$. For fitting, choose boron ($Z = 5$) and nitrogen ($Z = 7$). Using Table 1 we have for boron $y_1(5) = 3.00$, $y_2(5) = 12.7$, and for nitrogen $y_1(7) = 2.2$, $y_2(7) = 5.94$. Solutions of systems (6): $C_B = 0.407$ and (7): $C_B = 0.017$ do not match.

As can be seen from Table 2, the most acceptable coincidence of C1 and C_1' values was obtained for the Li–F system. Thus, the binary compound LiF was identified with an atomic concentration of lithium of 0.44–0.01.

4.3. Application

This method is very effective for detecting heavy impurities in a light matrix or light impurities in a heavy matrix.

On the calibration curve (Fig. 5) for standard samples of primary aluminum (light matrix), a linear dependence of the ratio of the intensities of Compton and Rayleigh peaks I_C/I_R on the aluminum content in the mass fraction range of 97.3–99.9 wt.% is observed.

According to this dependence, it is convenient to reject primary aluminum, avoiding the painstaking work of determining the concentration of all impurities. Indeed, with relative concentration sensitivity $\frac{1}{I}\frac{\partial I}{\partial C} = 2.5$ wt.% (Fig. 5) and the accuracy of measuring the ratio of intensities I_C/I_R of about 0.1 %, you can determine the purity of aluminum to a level of 99.95 wt.%.

As already noted, a quantitative analysis of the content of elements with $Z \le 9$ in heterogeneous samples presents significant difficulties due to the large dispersion of the calibration function, which is difficult to control experimentally. For example, the

Table 3. The calculated values of concentration sensitivity $\frac{1}{I_C/I_R}\frac{\partial(I_C/I_R)}{\partial C}$, %/(wt.%) when measuring light impurities in metals by the ratio of the integral intensities of the Compton and Rayleigh peaks

Metal	Ti	Fe	Ni	Zr	Nb	Ag	W
	Impurity						
H	16.52	20.70	22.30	125.25	153.88	?	?
He	3.63	3.95	4.02	5.68	5.74	6.50	11.66
Li	2.47	2.66	2.70	3.64	3.67	4.05	6.18
Be	2.16	2.32	2.36	3.15	3.18	3.49	5.14
B	1.96	2.12	2.16	2.89	2.92	3.20	4.64
C	1.89	2.05	2.09	2.83	2.85	3.13	4.51
N	1.70	1.85	1.90	2.58	2.60	2.86	4.09
O	1.55	1.70	1.75	2.40	2.42	2.65	3.78

calibration of Al–Al_2O_3 powder mixtures with respect to oxygen in the range of mass fractions of Al_2O_3 from 34 to 61 wt.% is characterized by a dispersion of 3.22 wt.%, which leads to low accuracy in measuring by the O–K_α line. This difficulty is overcome by measuring the ratio of the intensities of the Compton and Rayleigh peaks I_C/I_R (Fig. 6), which allows us to reduce the dispersion to 0.8 wt.%.

The prospects for applying the scattering method for the analysis of light impurities in metals are well illustrated by the data given in Table 3. So, for example, the accuracy of measuring the hydrogen content in niobium is 0.1 %/(53.8 %)/(% wt.)) = $6.5 \cdot 10^{-4}$ wt.% with the accuracy of measuring the peak ratio at a level of 0.1–0.2 %.

An experimental verification of the high sensitivity for determining the hydrogen content was performed on standard samples of a titanium-hydrogen binary system (Fig. 7). The obtained concentration sensitivity values of 170 wt.% were even higher than calculated, although the reason for this has not yet been clarified. Our measurements of standard titanium-hydrogen samples proved the possibility of determining hydrogen in titanium starting from 10^{-3} wt.% during no more than 5 min. For the Fe–C system, the concentration sensitivity value corresponds to the calculated one and amounted to 2.1 % per 1 % mass, which is quite sufficient for measuring carbon with an accuracy of 0.05 wt.%.

Thus, a quantitative determination of the content of light impurities, based on measuring the intensity ratio of the Compton and Rayleigh scattering peaks, is very promising due to the significant penetration depth of hard radiation into the sample (~ 0.1 to 1 mm) and the absence of artifacts associated with surface preparation.

A sharp increase in the dependence I_C/I_R with a decrease in the atomic number provides a unique opportunity to determine the light elements of the periodic system, including hydrogen; at this, the detection sensitivity is higher, the lower the atomic number of the element.

5. Conclusions

A generalization of the Compton method for identifying the composition of materials by the ratio of the intensities of incoherent and coherent scattering is proposed. The experimental dependence of I_C/I_R on the atomic number turned out to be the same for single-component and binary standards.

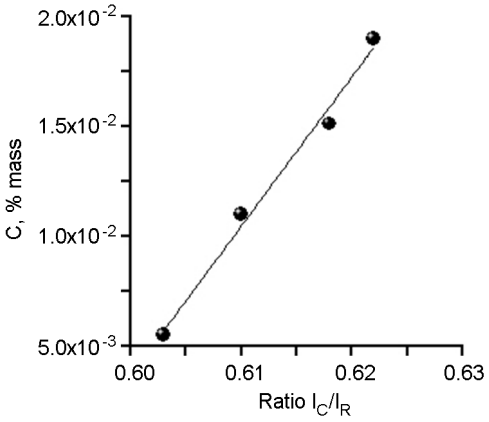

Fig. 7. Calibration function for standard samples of a binary titanium-hydrogen system.

This confirms the additivity of the contributions of various atoms to scattering for stoichiometric compounds. The form of the dependence is complex, but it is well described by the theoretical formula, with a correction for the difference in the absorption coefficients. When measuring this ratio under different registration conditions $x_1 = \sin\theta/\lambda = 0.831$ Å^{-1} and $x_2 = \sin\theta/\lambda = 1.297$ Å^{-1} for binary compounds, the value of effective atomic numbers $Z_{ef}(x_1)$ and $Z_{ef}(x_2)$ can be determined.

Using a system of linear equations taking into account $Z_{ef}(x_1)$ and $Z_{ef}(x_2)$, binary compounds based on chemical elements with $Z < 9$ can be identified. It is fundamentally important that this identification is possible in the absence of a relationship between the positions of the scattering peaks and the composition of the sample, and a qualitative and quantitative analyses of the composition of the material is carried out in the framework of solving one inverse problem. This is a difference from X-ray phase analysis based on the dependence of the position of diffraction peaks on the phase composition of the substance.

References

1. H.Ehrhardt, Rontgenfluoreszenzanalyse Anwendung in Betriebslaboratorien, VEB Deutscher Verlagfur Grundstoffindustrie Leipzig (1981).
2. A.H.Compton, *Phys. Rev.*, **21**, 483 (1923).
3. J.H.Hubbell, *Phys. Chem. Ref. Data*, **4**, 471 (1975).
4. J.H.Woo, *Phys. Rev.*, 27 (1926).
5. E.O.Wollan, *Phys. Rev.*, 43 (1933).
6. D.V.Rao, R.Cesareo, G.E.Gigante, *Phys. Scr.*, 50 (1994).
7. D.V.Rao et al., *Phys. Scr.*, 65 (2002).

8. C.C.Conti, M.J.Anjos, C.M.Salgado, *X-Ray Spectrom.*, **46**, 522 (2017).
9. Q.Zhang, Y.Guo, H.Bai et al., *X-Ray Spectrom.*, **47**, 4 (2018).
10. V.D.Hodoroaba, V.Rackwitz, *Anal. Chem.*. **86**, 6858 (2014).
11. A.Manjunath, B.R.Kerur, *Mater. Today: Proceed.*, **10**, 4134 (2016).
12. I.F.Mikhailov, A.A.Baturin, A.I.Mikhailov et al., *Rev. Sci. Instrum.*, **89**, 023103 (2018). DOI:10.1063/1.4993101
13. I.F.Mikhailov, A.A.Baturin, A.I.Mikhailov, S.A.Knyazev, X-Ray Spectrom., **48**, 604 (2019). DOI:10.1002/xrs.3033
14. H.M.Pirenne, The Diffraction of X-rays and Electrons by Free Molecules, Cambridge University Press, Cambridge (1946).
15. W.Heisenberg, *Phys. Zeitschr.*, **32**, 737 (1931).
16. P.Duvauchelle, G.Peix, D.Babot, *Nucl. Instrum. Meth. Phys. Res.*, 155 (1999).
17. R.W.James, in: the Crystalline State, ed. by L.Bragg, v.2, London (1950).
18. I.F.Mikhailov, A.A.Baturin, A.I.Mikhailov, S.V.Surovitskiy, *X-Ray Spectrom.*, **49**, 284 (2020). DOI:10.1002/xrs.3117S.S.