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The Total-Reflection X-Ray Fluorescence Yield Formed by a Waveguide Resonator under Conditions of Ion Beam Excitation

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Abstract—The features of methods for total-reflection X-ray fluorescence analysis with proton-induced X-ray fluorescence emission are described. A setup for obtaining X-ray fluorescence spectra under the conditions of proton-beam excitation has been developed using these methods. The setup is based on a specially designed planar X-ray waveguide resonator. The features of the new experimental diagnostic method in the unique research facility (UNU no. 45) of the Sokol-3 analytical ion-beam complex are discussed; some attention has been paid to the description of the capabilities of this facility.

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1. INTRODUCTION

X-ray fluorescence (XRF) analysis of materials under conditions of total external reflection (TR) of the exciting X-ray flux on a studied surface under is a standard and highly efficient method for elemental diagnostics of material samples that is based on measuring the X-ray fluorescence yield [1]. In the case of total external reflection, the incident flux of hard X-ray radiation (usually MoK_α , RhK_α , or AgK_α radiation) induces secondary X-ray fluorescence in the surface layer of a sample with a thickness of 3–5 nm, thus characterizing the elemental composition of this layer. Under these conditions, X-ray fluorescence spectra demonstrate an extremely low intensity of the background component and do not require the introduction of matrix corrections [2]. Moreover, a linear relationship between the intensity of the fluorescence lines and the concentration of the corresponding atoms in the excited surface layer is observed in the widest range of intensities.

Based on these features of the total-reflection X-ray fluorescence (TXRF) spectrometry, this method is considered as an effective means for quantitative elemental analysis of both solid and liquid materials by diagnosing their dry residues on polished Be

substrates. Due to the low background component, TXRF spectrometry is characterized by extremely low detection limits for impurities. At the same time, this method, like the entire XRF analysis of condensed samples, together with the fluorescence excitation by electron beams or X- and γ -ray fluxes, has substantial difficulties in diagnostics of the elemental composition by the yield of low-energy characteristic radiation. This primarily pertains to the definition of low- Z elements. This fact is illustrated in Fig. 1, which shows the excitation cross sections for the characteristic X-ray fluorescence of the K_α and L_α lines of various elements when MoK_α radiation flux is used as the exciting agent. A comparison of the excitation cross sections of the YK_α and AlK_α lines shows that this parameter for yttrium is greater than that for aluminum by four orders of magnitude.

This difficulty can be overcome by using the ion-beam excitation of X-ray fluorescence, i.e., the particle-induced X-ray emission (PIXE) method [3]. This is demonstrated in Fig. 2, which shows the energy dependences of the XRF excitation cross section for K_α lines of various elements when a hydrogen-ion flux is used as an excitation agent [4]. Comparison of the excitation cross sections for the YK_α and AlK_α lines

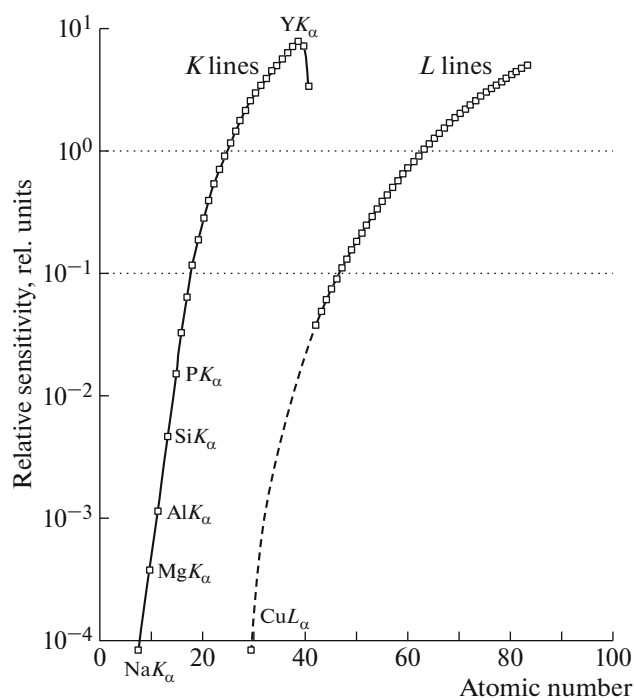


Fig. 1. The excitation cross sections for characteristic X-ray fluorescence of the K_{α} and L_{α} lines of various elements under exposure to MoK_{α} X rays.

according to the data shown in Fig. 2 for the hydrogen-ion flux with energy $E_0 = 1$ MeV shows that in this case the excitation cross section for aluminum is greater than that for yttrium by four orders of magnitude.

The ion-beam excitation of X-ray fluorescence is characterized by a significantly lower bremsstrahlung intensity compared to the use of electrons, which, in turn, guarantees a decrease in the background component. However, the PIXE method has its own drawbacks. First, the recorded X-ray fluorescence spectrum requires the introduction of matrix corrections, and, second, each measured line reflects the average elemental composition of the layer, whose thickness is determined by the absorption coefficient of quanta of this line in the studied material. Although the problem of introducing matrix corrections, especially for inhomogeneous materials, is difficult to solve, the problem of the dependence of the line intensities in an X-ray fluorescence spectrum on the absorption coefficients can be solved with ease.

2. THE SOKOL-3 ION-BEAM COMPLEX

The experimental investigations were conducted using one of the measuring chambers of the unique Sokol-3 research facility (UNU no. 45) [5]. This com-

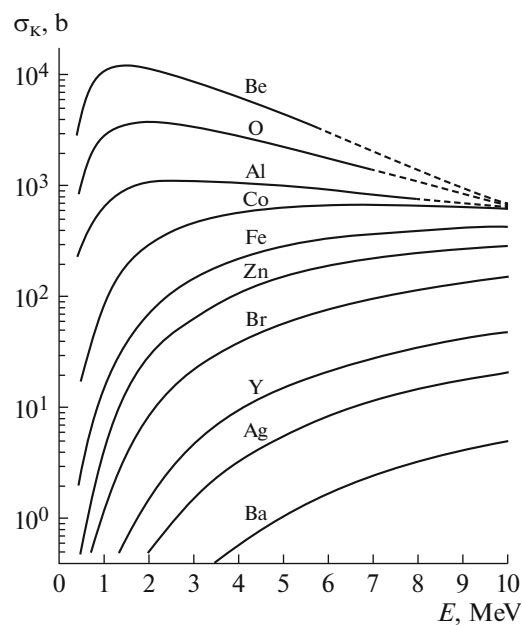


Fig. 2. The excitation cross sections for X-ray fluorescence of the K_{α} lines of various elements vs. the energy of hydrogen ions [4].

plex is based on the ESU-2 Van de Graaff electrostatic generator, which is designed for generating He^+ and H^+ ion fluxes of in the energy range $E_0 = 0.05\text{--}2.00$ MeV with a precision of 0.5 keV. The complex possesses all of the ion-beam analysis methods whose base is the Rutherford backscattering spectrometry (RBS) [6]. All ion-beam methods (RBS, XRF under ion excitation, nuclear reactions, recoil nuclei method, optical ionoluminescence, and ion channeling) are nondestructive, and the RBS is an absolute analytical method (that requires no standards and references). The detection limits of this method are at a level of 0.1 at %. However, the use of XRF methods with ion excitation and nuclear reactions makes it possible to lower this level to $(1\text{--}2) \times 10^{-6}$ at %. The ion-beam methods allow the determination of multielement concentration profiles along the depth with a depth resolution as high as 2 nm for surface layers with a thickness of up to 15 μm . The recoil nuclei method makes it possible to measure the depth distribution of hydrogen atoms [7] in the target under vacuum conditions (10^{-6} Torr). In general, the complex of ion-beam methods for analyzing materials is very efficient, but rather expensive and is almost not used in Russia.

Figure 3 shows a schematic diagram of the experimental chamber of the Sokol-3 complex. The chamber provides RBS measurements using the two-detector system and channel for XRF detection and measurements. Particular attention is paid to the placement of a compact X-ray detector cooled by a

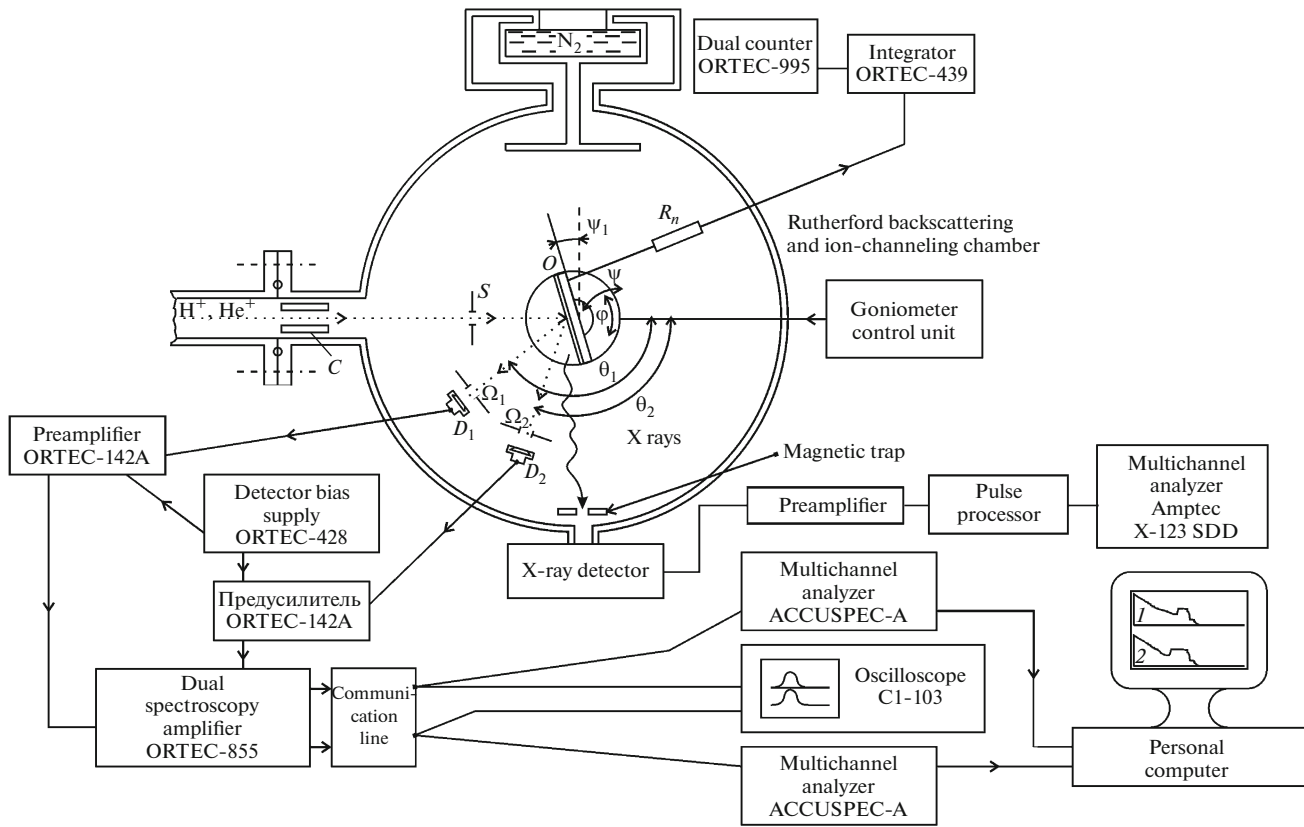


Fig. 3. The block diagram of the Sokol-3 unique research facility: (C) collimator, (S) shutter with an auxiliary collimator, (D) detector, (Ω) solid angle of the detector, (θ) ion scattering angles, and (ψ) angle of deviation from the normal.

Peltier microsystem inside the chamber. A vacuum flange with the X-ray detector placed inside is shown in Fig. 4. The detector holder is equipped with a heat sink and a magnetic trap with a split collimator. This design eliminates the incidence of scattered ions and knocked-

out electrons on the entrance window of the detector. The Amptec X-123 silicon drift detector is equipped with an 8- μm -thick entrance Be window, which provides detection of X-ray lines with $E > 0.5 \text{ keV}$ (in particular, the oxygen line with $E_{K\alpha} = 0.523 \text{ keV}$).

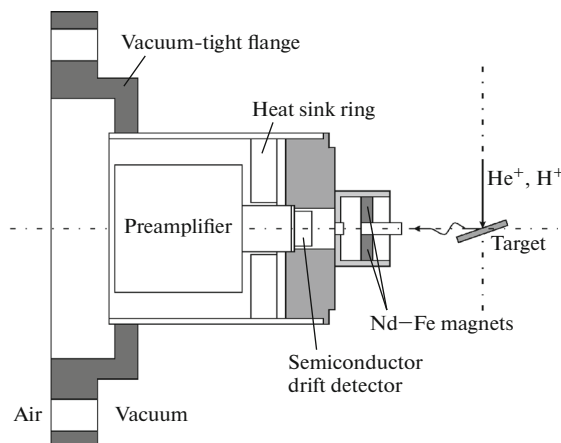


Fig. 4. The vacuum-tight flange with an X-ray detector installed in it.

3. A METHOD FOR DETECTING ION-INDUCED X-RAY FLUORESCENCE OF AN ULTRATHIN SURFACE LAYER

The layout for the detection of the X-ray fluorescence yield in a thin surface layer of the test sample is shown in Fig. 5. The conditions for transporting X-ray fluorescence radiation out of the surface layer are created by forming a waveguide-resonance slit clearance between the surfaces of the polished Be reflector and the sample. The width of this slit (150 nm) is formed by deposition of 150-nm-thick titanium strips on the edges of the Be reflector. At the center of the reflector is a hole for the passage of the ion beam towards the sample. The ion flux induces X-ray fluorescence of the target, regardless of the presence or absence of a beryllium reflector. At the same time, the waveguide-resonance slit captures only that characteristic radia-

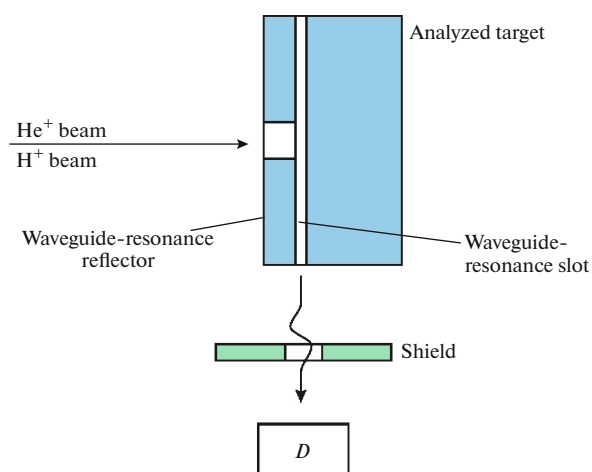


Fig. 5. The diagram of X-ray fluorescence yield in a thin surface layer of the test sample with total external reflection formed by the waveguide resonator. (D) detector.

tion of the sample that is experiencing TR from the Be reflector surface. The smallness of the TR angles guarantees that the X-ray fluorescence yield from deep layers of samples does not fall into the waveguide-resonance channel formed by the surfaces of the sample and the reflector [8]. Therefore, an X-ray fluorescence flux that is characteristic of the surface layer 3–5 nm in thickness is produced at the output of such a specific waveguide resonator similarly to the manner in which this takes place in TXRF spectrometry mea-

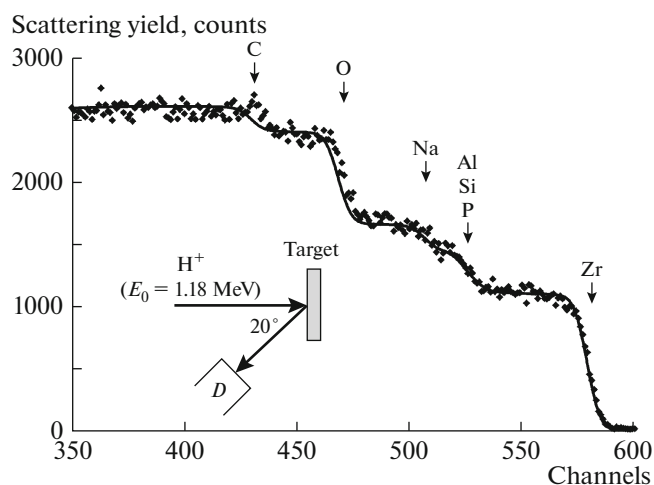


Fig. 6. The RBS spectrum of the multielement sample containing light elements, which was measured by one of the scattered-ion detectors in the experimental chamber of the complex. (D) detector.

surements. Performance of such measurements allows us to establish a new diagnostic method, i.e., ion-induced TXRF.

4. EXPERIMENTAL RESULTS

A multielement sample containing low-*Z* elements was chosen for the experimental investigations. Its composition was determined by approximating the

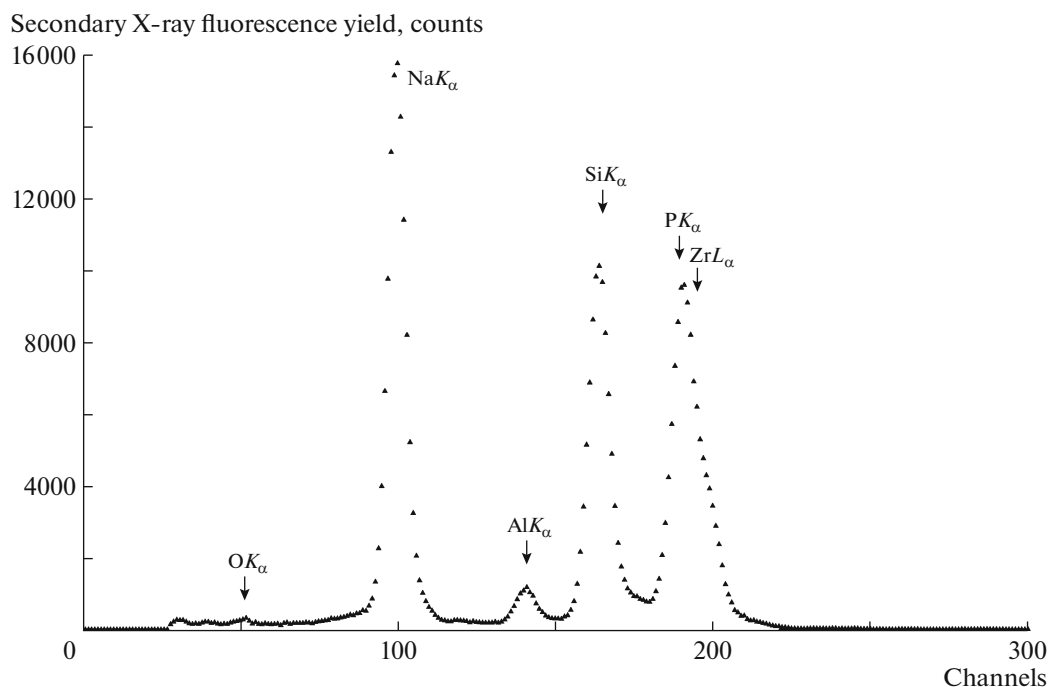


Fig. 7. The X-ray fluorescence spectrum of the $\text{Na}_3\text{Zr}_{1.3}\text{Si}_{1.9}\text{Al}_{0.1}\text{P}_1\text{O}_{12}\text{C}_2$ sample, obtained under proton excitation using a waveguide-resonance structure of a special design shown in Fig. 5.

RBS spectra of the H^+ ion flux ($E_0 = 1.18$ MeV). Figure 6 shows the RBS spectrum of this sample, which was measured by one of the scattered-ion detectors in the experimental chamber of the complex. The spectrum is a stepwise distributed array of experimental points (channels). The energy of scattered ions on the abscissa and the intensity of scattering is on the ordinate. The arrows indicate the energy of hydrogen ions scattered by atomic nuclei on the sample surface. The composition of the sample is $Na_3Zr_{1.3}Si_{1.9}Al_{0.1}P_1O_{12}C_2$. Its proton-induced XRF spectrum obtained using a waveguide-resonance structure of a special design (Fig. 5) is shown in Fig. 7. Intense NaK_α , AlK_α , SiK_α , PK_α , and ZrL_α XRF lines are observed in this spectrum. The two latter peaks are piled-up. In addition, a weak OK_α line is observed; its intensity is low due to the strong absorption in the material of the detector window.

The spectrum is characterized by a negligibly low intensity of the background component due to the uncertainty of the coherence length of bremsstrahlung. Its intensity turned out to be lower by two orders of magnitude relative to a similar spectrum obtained without using the waveguide-resonance structure. Thus, the detection limits of the new TXRF method with the ion excitation (TXRF PE) are lower at least by an order of magnitude relative to the standard PIXE technology. However, in contrast to the standard TXRF method, the new method still requires matrix corrections.

5. CONCLUSIONS

A brief description is presented of methods for elemental analysis of materials: TXRF and XRF with ion

excitation. The combination of these methods and inclusion of a specially designed X-ray waveguide resonator in the experimental setup has made it possible to develop a new experimental method of supersensitive surface element diagnostics of the material, which is especially attractive for the quantitative analysis of light elements.

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REFERENCES

1. Klockenkamper, R. and von Bohlen, A., *Total Reflection X-ray Fluorescence Analysis and Related Methods*, Hoboken, NJ: Wiley, 2015.
2. Van Grieken, R. and Markowicz, A.A., *Handbook of X-Ray Spectrometry*, New York: Marcel Dekker, 2002.
3. Johanson, S.A.E., Campbell, J.L., and Malquist, K.G., *Particle Induced X-Ray Emission Spectrometry (PIXE)* New York: Wiley, 1995.
4. Cahill, T.A., *Annu. Rev. Nucl. Part. Sci.*, 1995, vol. 30, p. 211.
5. Egorov, V.K., Egorov, E.V., and Afanas'ev, M.S., *Bull. Rus. Acad. Sci.: Phys.*, 2014, vol. 78, no. 6, p. 498.
6. Schmidt, B. and Wetzig, K., *Ion Beams in Material Processing and Analysis*, Wien: Springer, 2013.
7. Tirira, J., Serruys, Y., and Trocellier, P., *Forward Recoil Spectrometry, Application to Hydrogen Determination in Solids*, New York: Plenum, 1996.
8. Egorov, V.K. and Egorov, E.V., *Trends Appl. Spectrosc.*, 2010, vol. 8, p. 67.

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