

Ion-Beam and X-Ray Methods of Elemental Diagnostics of Thin Film Coatings

V. K. Egorov^{a,*}, E. V. Egorov^{a,b,c}, and M. S. Afanas'ev^b

^a *Institute of Microelectronics Technology Problems and High Purity Materials, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*

^b *Institute of Radioengineering and Electronics, Russian Academy of Sciences, Fryazino, Moscow oblast, 141190 Russia*

^c *Financial University under the Government of the Russian Federation, Moscow, 117303 Russia*

*e-mail: egorov@iptm.ru

Received July 16, 2019; revised July 16, 2019; accepted July 25, 2019

Abstract—We show how the combined use of the methods of Rutherford backscattering of ions and X-ray fluorescence analysis under conditions of total external reflection of the flow of exciting hard X-ray radiation and registration of the X-ray radiation output during ion excitation allows to effectively diagnose the elemental composition of thin-film coatings and films of dry residues of liquids. These methods and the features of their experimental application are briefly described. Examples of the complex methodological analysis of real objects are given. The possibility of increasing the efficiency of the methods of X-ray fluorescence analysis of materials due to the inclusion in the X-ray optical schemes of experimental measurements of flat X-ray waveguide resonators is indicated.

Keywords: Rutherford backscatter, X-ray fluorescence diagnostics, X-ray fluorescence analysis, thin-film coatings, films of dry solids

DOI: 10.1134/S1063783419120114

1. INTRODUCTION

The problem of effective elemental diagnostics of materials, along with their structural and phase analysis, is crucial in the search for new material structures with the necessary properties. This problem becomes especially relevant when developing protective and functional coatings, as well as when performing modification of the surface layers of materials by implantation and diffusion methods. In these cases, the zones of analytical interest are nanoscale. Besides, the formulation of the technological process often requires the applied analytical techniques to minimize the destruction of the diagnosed object, the expressivity of measurements, and ensure their quantification. In terms of methodological choice, the last requirement is especially important due to the lack of reliable standards in the diagnosis of nanoscale objects.

The only instrumental method (with the exception of weighing) that does not require the use of standards and references is well known to be Rutherford backscattering (RBS) of ions [1]. Based on first principles, this method allows approximating the obtained spectra with an accuracy of up to 1%. At the same time, the method is characterized by a rather low analytical sensitivity. When using it, the detection limits of impurity components are no better than 0.1 at %. Therefore, measurements using RBS spectrometry are useful for

quantitative diagnostics of the elemental content of structure-forming components, as well as, if necessary, determination of elemental concentration profiles over the thickness of film coatings and surface layers of bulk structures. To diagnose the presence of trace concentrations of modifying or random impurities in them, it is effective to use special methods of X-ray fluorescence analysis, which are realized upon ion-beam excitation of the characteristic X-ray fluorescence (PIXE) output [2], as well as when registering this output excited by a flow of hard X-ray radiation under conditions of its total external reflection on the surface of the object under study (XRF TER) [3]. The following experimental data show that the combined use of these three diagnostic methods allows the exhaustive quantitative control of the elemental composition of thin film coatings and thin surface layers of materials.

2. DIAGNOSTIC CAPABILITIES OF XRF TER SPECTROMETRY

X-ray fluorescence analysis of the elemental composition of materials is the most common method of such diagnostics. At the same time, the standard approach to the application of this method under the conditions of X-ray [4] and electronic [5] excitation of the characteristic X-ray fluorescence output charac-

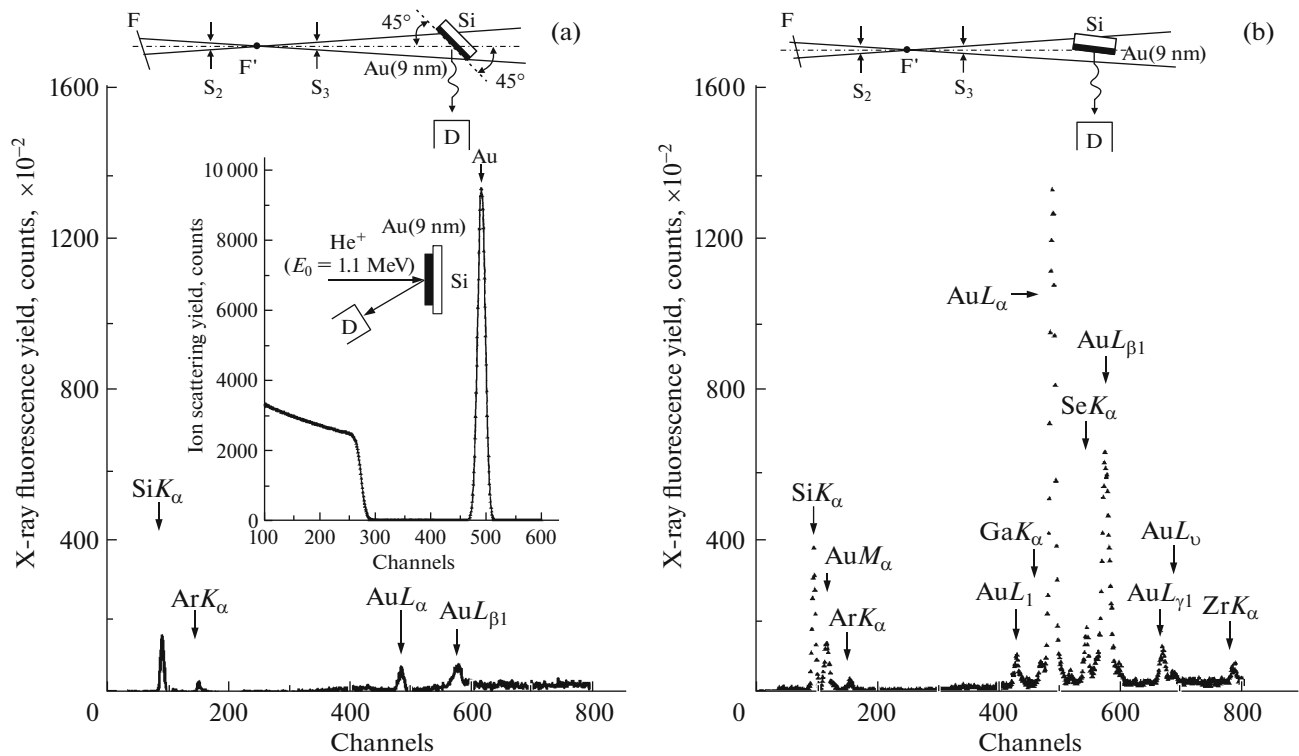


Fig. 1. X-ray fluorescence spectra of the Au (9 nm)/Si sample obtained (a) in the geometry of the XRF TER measurements and (b) under the conditions of standard XRF diagnostics recorded under identical operating conditions of the BSV-27 (Mo) radiation source and the excitation flow formation. The channel energy scale is 20 eV/channel. The inset shows the RBS spectrum of the studied sample.

terized by the incidence angle of the excitation flux to the surface of the object under study $\theta = 45^\circ$ and the selection of the analyzed flux corresponding to the same angle (Fig. 1a) has a number of analytical drawbacks. The most important of these is the presence of a “matrix effect” associated with the mutual influence of the X-ray fluorescence characteristic radiation excited in the object [6]. Besides, due to the sufficiently large thickness of the material layer excited in the research object (5–10 μm), the standard approach is characterized by a noticeable background component that is a critical parameter in determining the detection limits of impurity components [7]. Therefore, the use of X-ray fluorescence analysis in standard experimental geometry seems to be ineffective for the elemental diagnostics of thin-film coatings and near-surface layers of materials. The search for conditions for increasing the efficiency of such diagnostics led to the appearance of XRF TER spectrometry, i.e., the performance of X-ray fluorescence analysis under conditions of total external reflection of the excitation flux [8]. Under these conditions, the thickness of the excited surface layer of the studied object decreases to 3–5 nm, which, in turn, eliminates the matrix effect on the recorded spectrum and allows reducing the value of the background contribution. As a result, the detection limits of the method are reduced to 1 ppm.

Besides, the excitation of the surface layer of the studied object under the conditions of XRF TER measurements is more effective. As a result, the intensity of characteristic lines in comparison with the standard geometry of the XRF measurements increases sharply. This is well illustrated in Fig. 1 representing the XRF and XRF TER spectra obtained for thin-film gold coatings on silicon. The RBS spectrum of this coating is also shown in the figure.

Since a thin near-surface layer of the studied object is excited in XRF TER spectrometry, the critical parameter of the method is the value of the radiation density of the excitation flux. An increase in the efficiency of XRF TER measurements by increasing this parameter can be achieved either by due to a primitive increase in the power of the radiation source or by searching for original solutions of the concentration of the radiation flux. A similar solution was found in the framework of the development of a specific device for X-ray nanophotonics, i.e., a plane X-ray waveguide-resonator (PXRWR) [9]. This device allows the formation of filamentary X-ray fluxes with a nanoscale width at an increase in the radiation density of the generated flux, which exceeds this parameter in the fluxes formed by cutting slots by 3–4 orders of magnitude. As a result, the use of these devices allowed lowering the

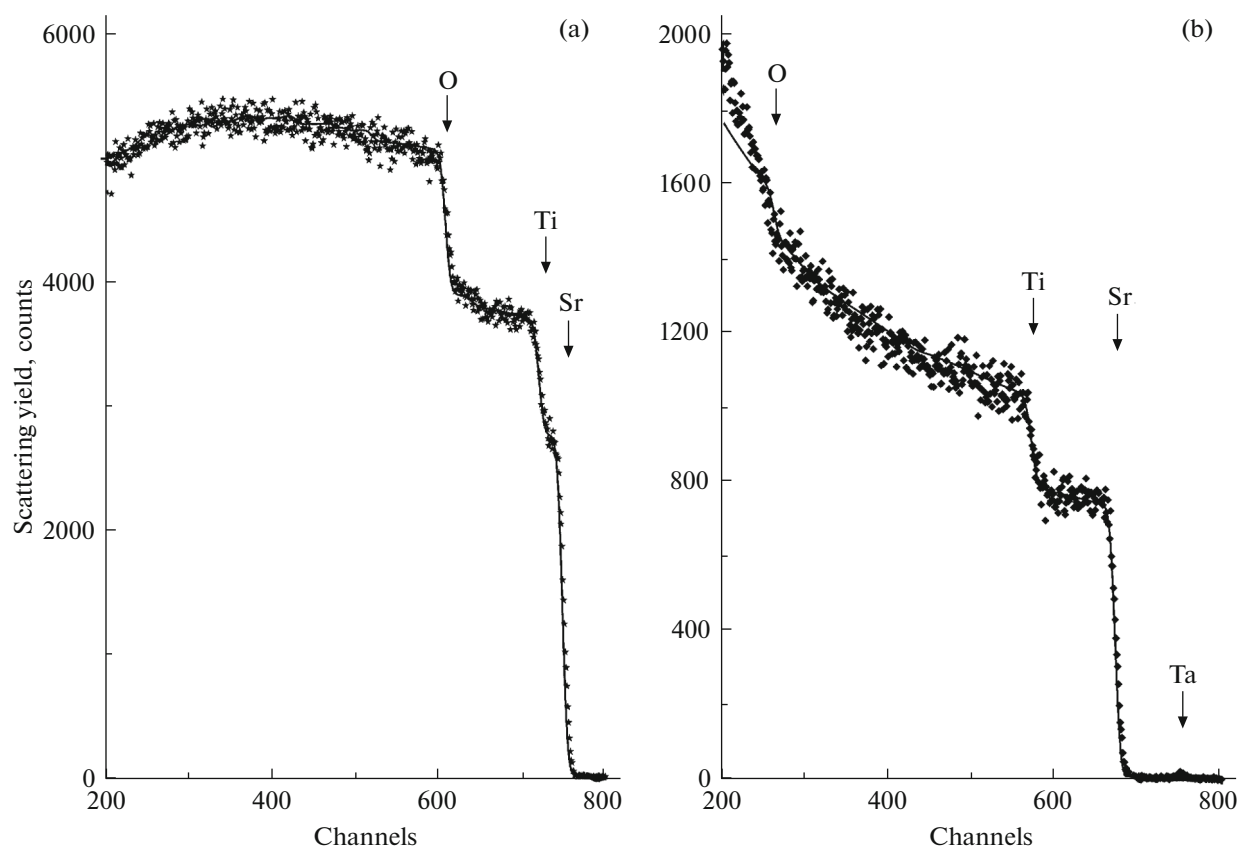


Fig. 2. RBS spectra of (a) He⁺ and (b) H⁺ ion fluxes recorded for a SrTiO₃ single crystal in its random orientation with respect to the propagation direction of ion beams.

limits for the impurities detection in the XRF TER spectra by two more orders of magnitude [10, 11].

XRF TER measurements can be performed either using specialized facilities [12] or as part of small-angle measurements using standard X-ray diffractometers with the inclusion of an energy-dispersive spectrometer in the measuring system [13]. Since the thickness of the excited layer in XRF TER spectrometry is 3–5 nm, the surface of the studied object should be flat with a low level of waviness and roughness.

3. FEATURES OF ION-BEAM DIAGNOSTICS OF MATERIALS

The most important method of ion-beam diagnostics of materials is Rutherford backscattering of ion beams on the nuclei of atoms that compose material objects [14]. Computer approximation of experimentally obtained RBS spectra allows obtaining quantitative data on the content of structure-forming elements of the studied material. Typically, RBS diagnostics of materials use beams of helium and hydrogen ions with an energy of 1–3 MeV. Since long-term exposure to ion beams leads to structural distortions and even amorphization of the structure of materials, the ana-

lytical application of ion-beam diagnostics is limited by low dose loads, usually not exceeding $(3-5) \times 10^{14}$ ions/cm². Unlike the XRF TER measurements, RBS studies, as well as X-ray fluorescence analysis upon ion excitation, are performed in vacuum chambers. The registered spectra are normalized based on the number of ions scattered during the measurement session.

Figure 2 shows the RBS spectra of the fluxes of He⁺ and H⁺ ions obtained for the SrTiO₃ single crystal in the position of its random orientation relative to the direction of propagation of ion fluxes. The approximation of the spectra performed using the RUMPP computer program (an upgraded version of the RUMP program [15]) showed the stoichiometry of the studied object. In this case, the approximation of the RBS spectrum of the hydrogen ion flux required additional measurements due to the non-Rutherford contribution to the scattering of these ions by the nuclei of oxygen atoms [16]. The concentration of structural impurities in the studied single-crystal sample was determined on the basis of data obtained by the methods of XRF TER and XRF upon ion excitation. The spectra recorded by these methods are shown in Fig. 3.

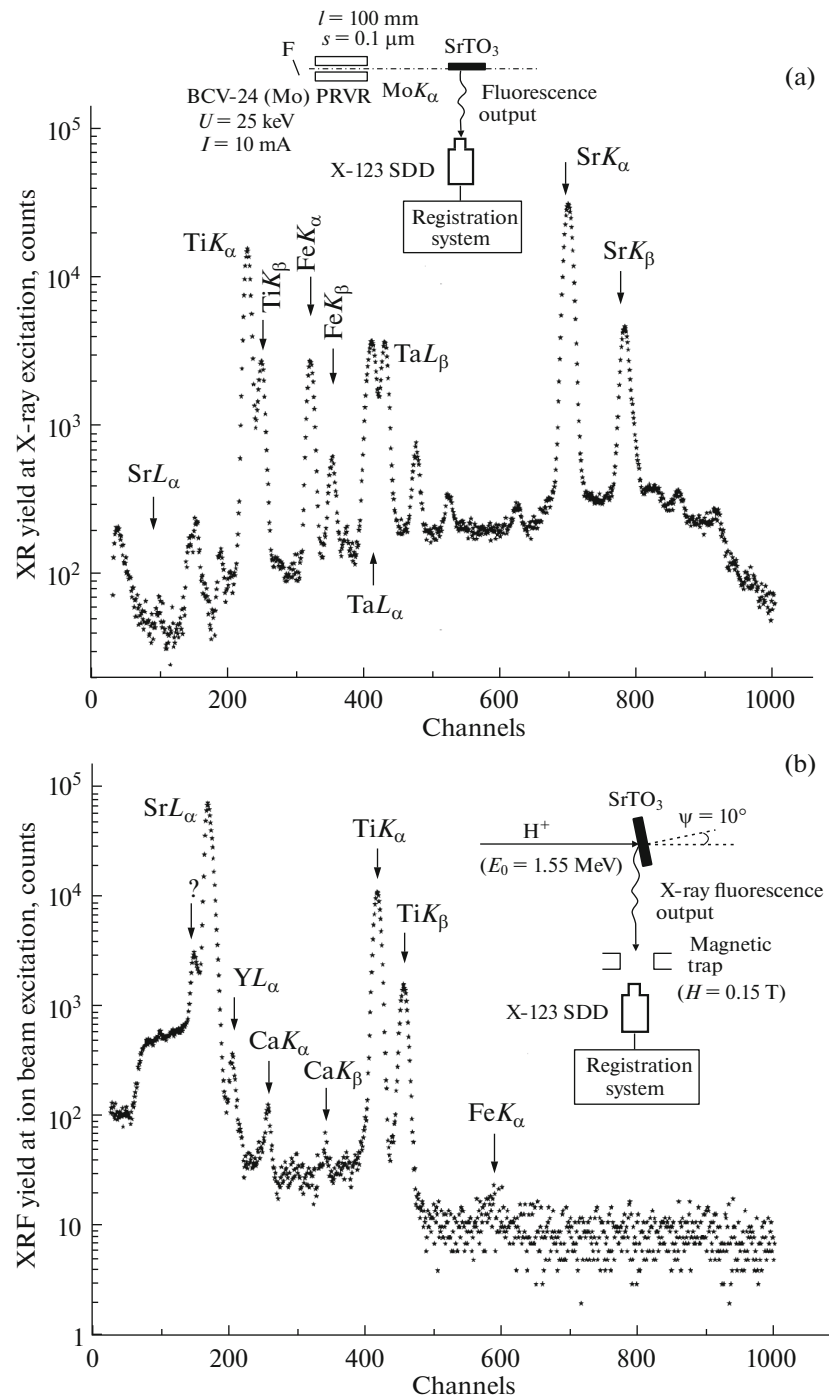


Fig. 3. (a) XRF TER and (b) PIXE spectra obtained for the SrTiO_3 single crystal. The channel energy scale is 20 eV/channel for XRF TER measurements and 10 eV/channel for PIXE measurements.

They show that the main impurities in this sample are Fe and Ta.

When comparing the X-ray fluorescence spectra shown in Fig. 3, it is noteworthy that the spectrum recorded in the geometry of the XRF TER measurements shows a high intensity for the $\text{Sr}K_\alpha$ lines ($E =$

14.164 keV) and an extremely low output for the $\text{Sr}L_\alpha$ line ($E = 1.806$ keV). At the same time, the XRF spectrum recorded under excitation by a proton beam with an energy of $E = 1.07$ MeV shows an extremely high intensity for the $\text{Sr}L_\alpha$ line in the absence of a recorded intensity for the $\text{Sr}K_\alpha$ line (the corresponding energy

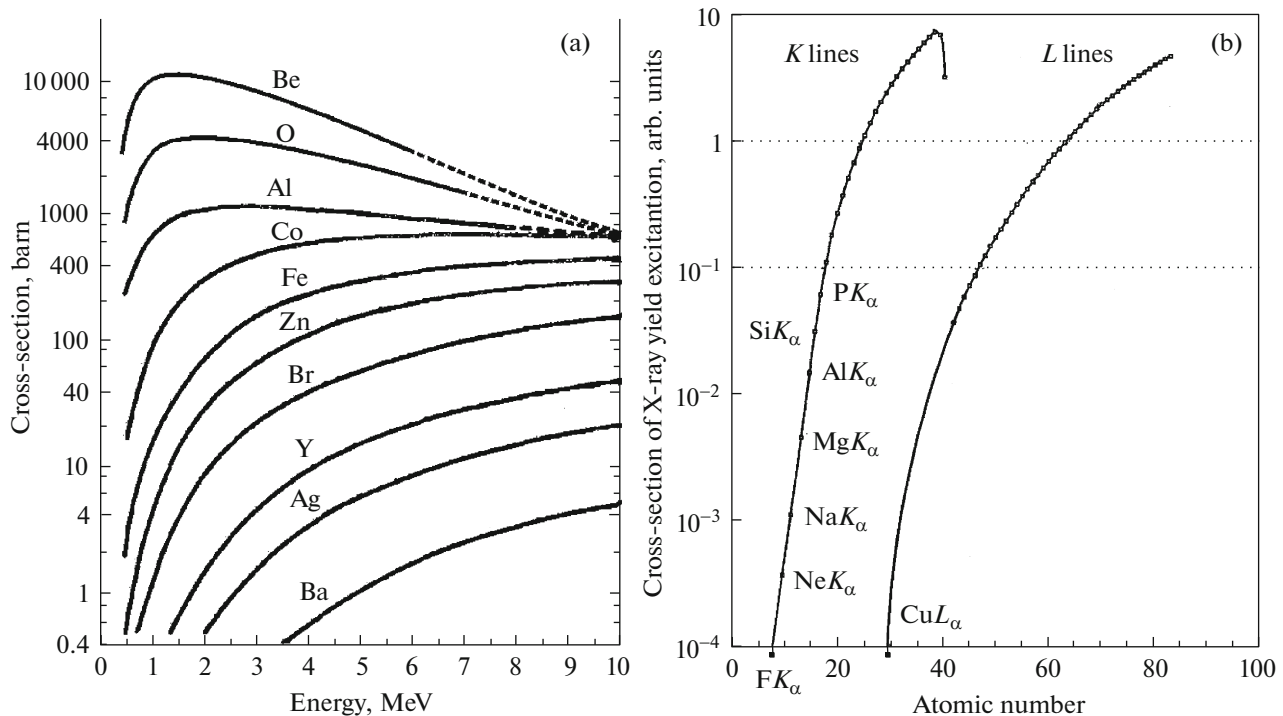


Fig. 4. Cross sections for the excitation of X-ray fluorescence by (a) proton beams of various energies [18] and (b) a molybdenum radiation flux generated by a PXRWR with a slit width of 100 nm using a BSV-27 (Mo) radiation source in the $U = 25$ keV, $I = 10$ mA mode.

interval is not shown in Fig. 3b). The intensity of the Ti K_{α} line ($E = 4.51$ keV) in both spectra shows an intermediate value. In general, a comparison of these spectra is confirmed by the fact that the use of electron, X-ray, and gamma-ray excitation of characteristic X-ray fluorescence is more effective for searching in output spectra of high-energy lines [17] while the lines corresponding to low-energy atomic emissions are more efficiently excited by ion beams [18]. Comparative data on the excitation cross sections for the X-ray fluorescence output by the proton beam and the Mo K_{α} radiation flux formed by the planar X-ray waveguide-resonator are shown in Fig. 4 [19]. Comparison of the presented dependences shows that X-ray fluorescence analytical methods implemented under conditions of total external reflection and ion-beam excitation are not competing approaches, but constitute a superb complement to each other. However, it should be noted that these methods characterize the excitation of spatially noncoincident volumes of the studied object. XRF TER measurements allow estimating the elemental composition of the surface layer of this object with a thickness of 3–5 nm averaged over its entire surface area. At the same time, under conditions of ion-beam excitation of X-ray fluorescence, the output of characteristic lines is formed in the cylindrical volume of the material that is determined by the cross section of the ion beam (usually

about 1 mm in diameter) and its penetration depth (from 2 to 20 μm , depending on the type and energy of ions in the beam and the density of the diagnosed material). In this case, the ion-beam excitation method is not without the influence of the matrix effect, as well as the dependence of the intensity of the recorded X-ray fluorescence lines on their absorption coefficient in the material. Due to these factors, the method can be considered semiquantitative only. At the same time, it significantly exceeds the XRF TER capabilities in sensitivity in the energy range of 0.5–5.0 keV, and when using X-ray waveguide-resonance structures, it is capable of competing in sensitivity with the methods of mass spectrometric elemental diagnostics [20]. This is well illustrated by the experimental data presented in Fig. 5. The figure illustrates the comparative characteristic of X-ray fluorescence spectra obtained by the methods discussed above, which reflect the content of impurity elements in a sample of heavy oil, the film of which was deposited on a Be substrate. The inset shows the RBS spectrum of the hydrogen ion beam for this film sample, based on which the oil macrocomposition of $\text{H}_{0.1}\text{C}_{0.87}\text{S}_{0.028}\text{N}_{0.002}$ was determined. The hydrogen content in the sample was determined by the method of recoil nuclei [21]. Table 1 shows the elemental composition of the impurity content in the oil sample relative to the content of sulfur atoms in it. An inter-

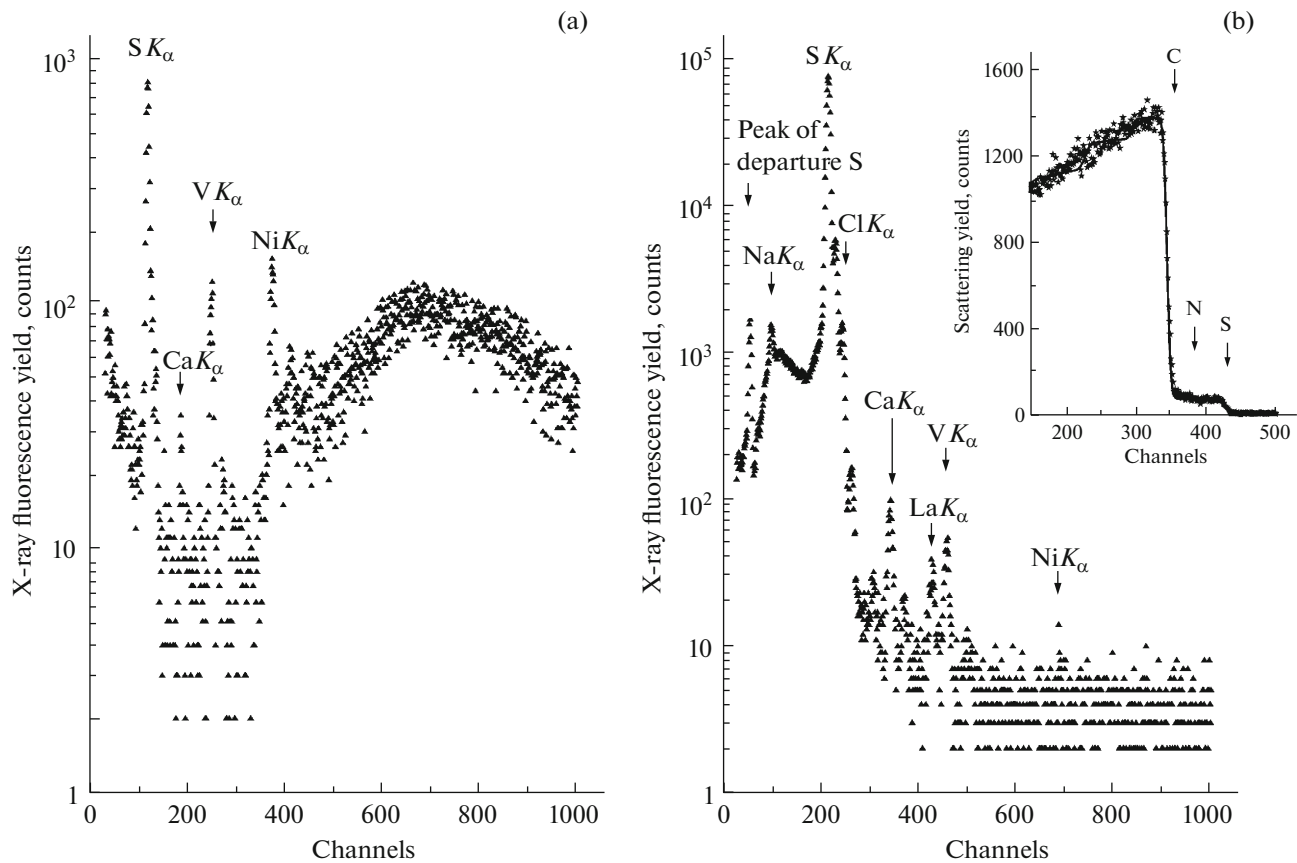


Fig. 5. (a) PIXE and (b) XRF TER spectra obtained for a heavy oil film deposited on a Be substrate. The channel energy scale is 10 eV/channel for spectrum (a) and 20 eV/channel for spectrum (b). The inset shows the RBS spectrum of the studied sample.

esting result of the performed measurements is the diagnosis of the presence of industrially allocated amounts of vanadium and the fundamentally diagnosed presence of lanthanum atoms. The obtained data provided the basis for a comprehensive elemental diagnosis of products at all stages of oil cracking to identify the concentration processes of rare and rare earth elements.

The complex of ion-beam and X-ray fluorescence diagnostics may be successfully applied to solve a number of medical and biological problems, as well as to study multilayer thin-film objects [22], implantation [23] and diffusion structures [24], and to study the density defect of thin-film coatings.

Table 1. Obtained on the basis of XRD data, the content of impurity elements in a sample of heavy oil relative to the concentration of sulfur atoms in it

| S | Na | Cl | Ca | V | Fe | Ni | La |
|---|-------|-------|-------|-------|-------|-------|--------|
| 1 | 0.005 | 0.005 | 0.005 | 0.015 | 0.001 | 0.005 | 0.0005 |

4. CONCLUSIONS

The experimental data presented in this study give reason to expect that the combined use of ion-beam and X-ray fluorescence diagnostics of materials is a necessary and sufficient tool for the elemental characterization of thin-film coatings of the surface layers of the studied objects and films of dry residues of liquids.

ACKNOWLEDGMENTS

The authors thank the RAS academician Yu.V. Gulyaev for his interest in our work.

FUNDING

The work was performed as part of the State assignment no. 075-00475-19-00 and was partially supported by the Russian Foundation for Basic Research, project nos. 19-07-00271 and 18-029-11029.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. J. R. Bird and J. S. Williams, *Ion Beams for Material Analysis* (Academic, Sydney, 1989).
2. S. A. E. Johanson, J. L. Campbell, and K. G. Molquist, *Particle Induced X-Ray Emission Spectrometry (PIXE)* (Wiley, New York, 1995).
3. R. Klockenkamper and A. von Bohlen, *Total Reflection X-Ray Fluorescence Analysis and Related Methods*, 2nd ed. (Wiley, New York, 2015).
4. N. F. Losev, *Quantitative X-Ray Fluorescence Analysis* (Nauka, Moscow, 1969) [in Russian].
5. *Quantitative Electron-Probe Microanalysis*, Ed. by V. D. Scott and G. Love (Wiley, New York, 1983).
6. E. P. Bertin, *Principles and Practice of X-Ray Spectrometric Analysis*, 2nd ed. (Plenum, New York, 1975).
7. R. Jenkins, R. W. Gould, and D. Gedcke, *Quantitative X-Ray Spectrometry* (Dekker, New York, 1995).
8. Y. Yoneda and T. Horiuchi, *Rev. Sci. Instrum.* **42**, 1069 (1971).
9. V. K. Egorov and E. V. Egorov, *X-ray Spectrom.* **33**, 360 (2004).
10. V. K. Egorov, E. V. Egorov, and E. M. Luk'yanchenko, *Nanoinzheneriya* **5**, 7 (2015).
11. V. K. Egorov, E. V. Egorov, and E. M. Loukianchenko, *Asp. Min. Min. Sci.* **2**, 1 (2018).
12. H. Stosnach and A. Gross, *Lab. Report XRF 458* (Bruker AXS Inc., Berlin, 2015).
13. <https://www.amptek.com/products/sdd-x-ray-detectors-for-xrfeds/x-123sdd-complete-x-ray-spectrometer-with-silicon-driftdetector-sdd>.
14. M. Nastasi, J. W. Mayer, and Y. Wang, *Ion Beam Analysis, Fundamentals and Application* (CRC, Boca Raton, FL, 2015).
15. L. R. Doolittle, *Nucl. Instrum. Methods Phys. Res.* **9**, 344 (1985).
16. E. Rauhala, *Nucl. Instrum. Methods Phys. Res.* **12**, 447 (1985).
17. *X-ray Spectrometry: Recent Technological Advances*, Ed. by K. Tsuji and R. van Grieken (Wiley, Chichester, 2004).
18. T. A. Cahill, *Ann. Rev. Nucl. Part. Sci.* **30**, 211 (1980).
19. *Ion Beam for Material Analysis: Conventional and Advanced Approaches*, Ed. by I. Ahmad and M. Maaza (Intechopen, London, 2018), p. 38.
20. V. K. Egorov, E. V. Egorov, and M. S. Afanas'ev, *J. Phys.: Conf. Ser.* **1121**, 1 (2018).
21. H. Hofsas, *Forward Recoil Spectroscopy* (Plenum, New York, 1996).
22. *Handbook on Modern Ion Beam Material Analysis*, 2nd ed., Ed. by Y. Wang and M. Nastasi (Mater. Res. Soc., Warrendale, 2009).
23. *Ion Implantation*, Ed. by M. Goorsky (Intech, Rijeka, 2012).
24. P. L. Clay, E. B. Baxter, and D. I. Cherniak, *Geochim. Cosmochim. Acta* **74**, 5906 (2010).

Translated by A. Ivanov