

Elemental Analysis of Materials by Methods of Ion-Beam Diagnostics

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Abstract—A brief description of the ion-beam analytical complex used for the work is given. The possibilities of elemental analysis of the materials as a result of using the methods of Rutherford ion backscattering and X-ray fluorescence under ionic excitation are shown. A brief description of these methods and the conditions for their implementation is given. It is shown that the highest efficiency of elemental analysis is achieved when they are applied together. Experimental data showing the efficiency of using such an analysis in diagnostics of the elemental composition of residues of dry liquids and solid materials, including thin-film ferroelectric films, are presented.

Keywords: Rutherford backscattering, X-ray fluorescence analysis under ion excitation, complex analysis, ferroelectric film, PIXE

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INTRODUCTION

Ion-beam diagnostics of the elemental composition of materials is widely used in experimental analytical practice abroad [1]. Among them, the most widespread are: the Rutherford backscattering (RBS) of ions and X-ray fluorescence analysis under ionic excitation (Particle-induced X-ray emission (PIXE)).

The RBS method is the main method for the elemental diagnostics of multicomponent materials, including ferroelectric materials. To perform quantitative analysis of the elemental composition of a substance, the RBS method does not require the use of standards and etalon. The main application of the method is determination of the elemental concentration profiles over the film thickness with a depth resolution of 10 nm (under special conditions up to 2 nm). The method is multielement and allows one to determine the depth elemental concentration profiles and the total content of elements from lithium to uranium. The method is independent to the degree of electrical conductivity of the objects under study and is free from the influence of matrix effects. However, it is characterized by a low sensitivity with the detection limits detection of impurity elements at the level of 0.1 at %. This disadvantage is compensated by the parallel appli-

cation of the PIXE method. Its limits of detection for impurities vary in the range of 10^{-6} – 10^{-8} at % depending on the type of determined elements and the energy of the exciting ion flux. The method is semi-quantitative due to the influence of the matrix factor on the results of analysis. From the point of view of the diagnostics of ultralight elements, its capabilities are limited by the factor of the absorption of low-energy X-ray radiation by the material of the entrance window of the X-ray detector. In the case of a detection use with a Be window, the PIXE method makes it possible to diagnose all atoms in materials, starting with fluorine. To implement the method, ion beams with an energy of more than 1 MeV are required. In comparison with the method of the electronic excitation of X-ray fluorescence, PIXE is characterized by a significantly lower contribution of the background component due to the lower probability of the excitation of bremsstrahlung photons. Comparison of the capabilities of these methods gives grounds to assert that their combined use can significantly reduce the detection limits of impurity elements.

The aim of this work is to assess the possibilities of the combined use of the RBS and PIXE methods for

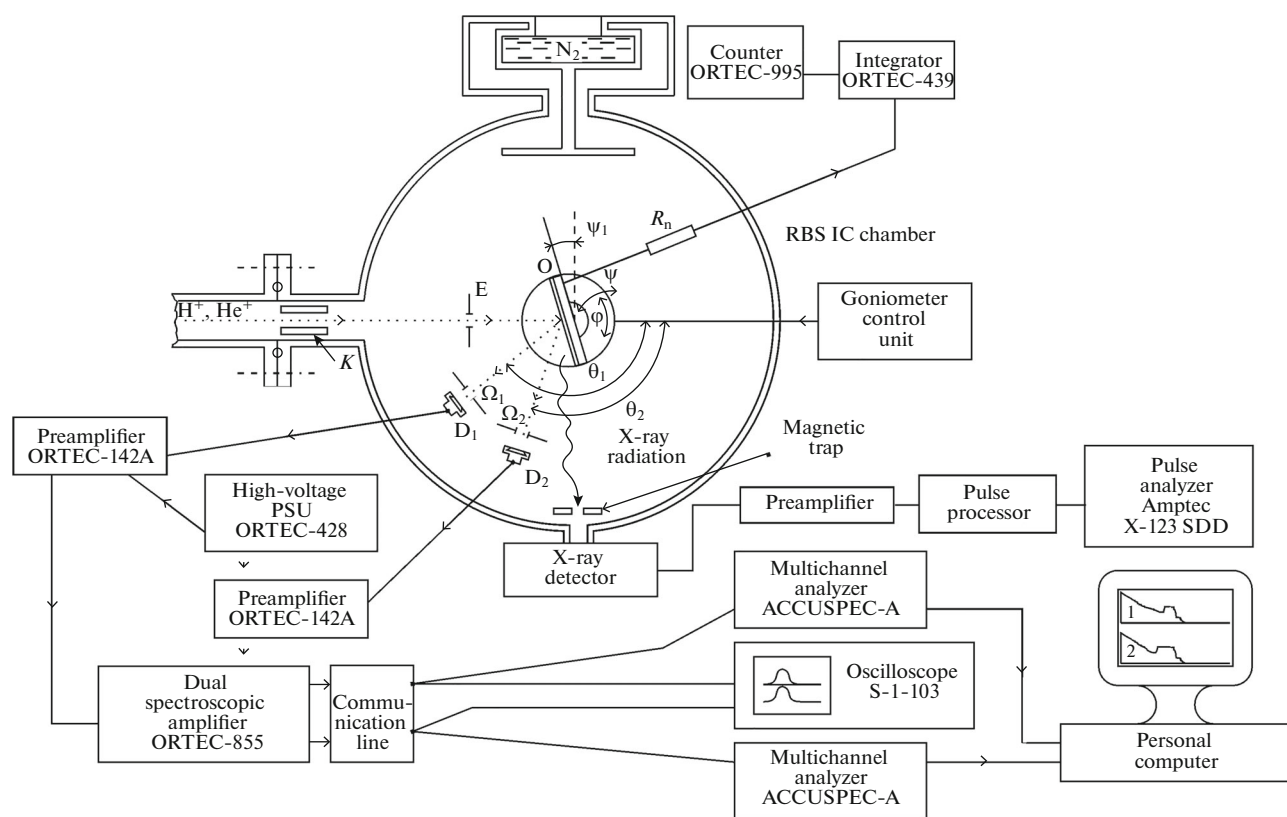


Fig. 1. Schematic representation of the Sokol-3 Rutherford backscattering chamber with two detector systems for collecting ion-scattering information and a recorder of X-ray fluorescence output under ionic excitation.

characterizing residues of dry liquids and solid materials in the form of ferroelectric films.

EXPERIMENTAL

All methods of the ion-beam analysis of materials are implemented under medium vacuum conditions (10^{-5} – 10^{-6} Torr or 10^{-3} – 10^{-4} Pa). To create such conditions, all ion-beam complexes are equipped with analytical chambers, an example of which is shown in Fig. 1. All such chambers are equipped with a collimator that shapes the size and form of the ion beam incident on the sample under study, a goniometer that allows this sample to be oriented relative to the direction of beam propagation, and a current integrator that records the total number of ions scattered during measurements. Since the chamber, the diagram of which is shown in Fig. 1, is oriented to parallel studies of materials by the RBS method and X-ray fluorescence analysis under ion excitation, detectors to record scattered ions (D_1 , D_2) and an X-ray detector are installed in the chamber. X-ray fluorescence and Rutherford spectra are recorded to computer memory and further processed using computer software [2, 3]. The ion-scattering system has two detectors located at different

angles to the direction of propagation of the ion beam. As a result, after performing the measurements, the experimenter has two RBS spectra corresponding to the same distribution of elements over the target thickness, obtained for different angles of ion scattering. Fitting these spectra with the available software avoids possible interpretation errors. At the same time, based on RBS measurements, there is no possibility of recording the presence of low-concentration impurities in the sample under study. In this case, the parallel recording of X-ray fluorescence spectra excited by an ion beam assists.

RESULTS AND DISCUSSION

Figure 2 shows the results of complex application of the RBS and PIXE methods. The right side of this figure shows the experimental and theoretical spectra of the RBS flux of hydrogen ions scattered at a heavy-oil film deposited onto a polished Be substrate. The precipitated oil sample was characterized by a high viscosity. As a result, the film thickness turned out to be more than $10\ \mu\text{m}$ and did not drip from the substrate surface during measurement procedure. Theoretical approximation of the experimental spectrum was per-

formed using the RUMPP computer program, which is a modern modification of the well-known RUMP program [4]. The approximation took into account the factor of nonRutherford scattering, which is characteristic of carbon atoms [5]. The spectrum consists of two steps corresponding to the presence of sulfur and carbon atoms in the volume of the oil sample. The small complication during the first stage is associated with the presence of a small amount of nitrogen in the film. Since the RBS measurements do not allow direct detection of the presence of hydrogen atoms in the sample, its content was determined by the method of recoil nuclei [6, 7]. In terms of the macro-content of elements, the composition of oil corresponds to the formula $H_{0.07}C_{0.90}S_{0.028}N_{0.002}$. At the same time, it was of interest to find out the composition of impurities in the oil film under study. These studies were carried out on the basis of a semi-quantitative approximation of the PIXE spectrum recorded in the parallel mode. This spectrum is shown on the Fig. 2b. The X-ray fluorescence lines of nitrogen and carbon are not represented in the spectrum due to their complete absorption in the material of the beryllium window of the X-ray detector. There is also a high-intensity peak for sulfur and a number of low-intensity peaks reflecting the presence of impurity atoms in the oil sample. Table 1 shows their approximate relative content, with the content of sulfur atoms in the sample taken as the reference point.

The results obtained were of interest due to the presence of vanadium and lanthanum atoms in heavy oil. Further research showed that the waste piles of oil refining also contained these elements.

Figure 3a shows the RBS spectrum of He^+ of a ferroelectric film on a silicon substrate, recorded by a detector corresponding to the scattering angle $\theta_1 = 160^\circ$. Films of the composition $Ba_{0.8}Sr_{0.2}TiO_3$ were obtained by the method presented in [8, 9]. The spectrum contains two relatively well resolved maxima, a step and an additional maximum on the inclined plateau of the step. In addition, at the base of the step, there is a certain elongation towards higher energies. The approximate processing of the spectrum showed that the intense peak in the high-energy region is the result of the scattering of He ions⁺ at the nuclei of Ba and Sr atoms distributed over the entire thickness of the coating, a small peak with a flat top corresponds to scattering at the nuclei of Ti atoms, also distributed over the entire thickness of the film. The step observed in the spectrum reflects the scattering of helium ions at atomic nuclei of the silicon substrate. The weak peak on the step plateau is the result of scattering at the nuclei of oxygen atoms distributed over the entire thickness of the ferroelectric film. The presence of a

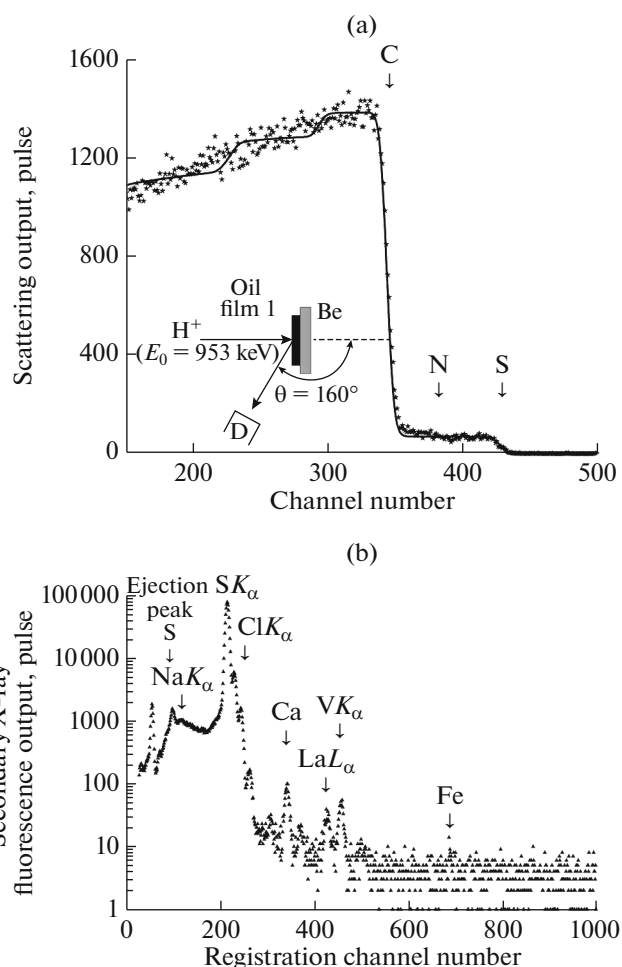


Fig. 2. Experimental spectrum of RBS H^+ ($E_0 = 0.953$ MeV) (a) and XRF spectrum (b) for an oil film deposited onto a polished beryllium substrate. The energy cost of the channel is 1.9 keV/channel and 10.8 eV/channel, respectively.

“tail” at the foot of the step is associated with the diffusion of silicon atoms into the film, and their penetration is observed throughout the entire thickness of the film. The presence of obvious asymmetry in the shape of the peaks corresponding to scattering at the nuclei of heavy atoms indicates the presence of some inhomogeneity of the coating composition over its thickness. It was possible to represent the model distribution of elements in the film coating in the form of two successive layers with a slightly different elemental

Table 1. Relative content of impurity elements in a sample of heavy oil

Element	Na	Cl	Ca	V	Fe	Ni	La	S
Content	0.005	0.005	0.005	0.015	0.001	0.0005	0.0005	1

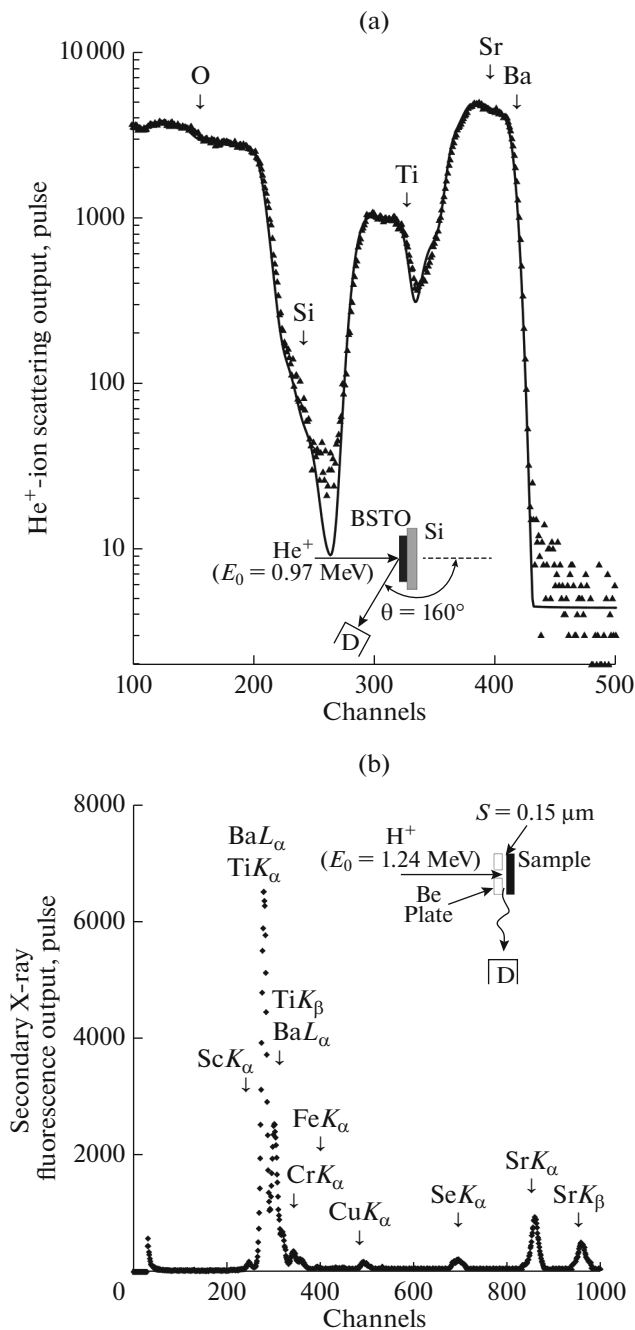


Fig. 3. Experimental RBS spectrum of He^+ ($E_0 = 0.97$ MeV) (a) and the PIXE spectrum (b) of a ferroelectric film formed on a silicon substrate. The survey geometry is shown in the figure. The energy cost of the channel is 1.9 keV/channel and 16 keV/channel, respectively.

composition (Table 2). The accuracy of determining the composition was 0.01.

The total thickness of the ferroelectric film is 90 ± 5 nm. The film is characterized by the presence of a certain amount of Si impurity atoms and an increased oxygen content in comparison with the assumed stoichiometry. During deposition of the film, a buffer oxide layer appeared on the surface of the Si substrate, which ensured subsequent growth of the ferroelectric film. The performed approximation of the spectrum shown in Fig. 3a, made it possible to reveal diffusion contamination of the ferroelectric film by atoms of the silicon substrate.

Figure 3b shows the PIXE spectrum obtained for the investigated ferroelectric film. The spectrum contains lines of the main structure-forming elements (TiK_α , BaL_α , BaL_β , SrK_α), as well as the line ArK_α . The main impurity elements are Ca, Sc, Cr, Mn, Fe, Ni, Cu, Zn and Se. It was found that the total concentration of impurities does not exceed 1 at %.

CONCLUSIONS

The paper shows the result of combined use of the RBS and PIXE methods, which illustrate the study of dry liquids in the form of a film of oil and solid materials in the form of a ferroelectric film.

The relative content of impurity elements in the sample of heavy oil has been determined.

The concentration profiles of the distribution of structure-forming elements over the thickness of the ferroelectric film have been determined.

It is shown that when a ferroelectric film is deposited onto a silicon substrate, the diffusion penetration of substrate atoms into the film is observed.

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Table 2. Model of the distribution of elements over the thickness of a ferroelectric film on a silicon substrate

Layer no.	Layer thickness, nm	Elemental composition, averaged over layer volume
1	20 ± 2	$\text{Ba}_{0.75}\text{Sr}_{0.12}\text{Ti}_{0.24}\text{O}_{3.4}\text{Si}_{0.10}$
2	70 ± 2	$\text{Ba}_{0.72}\text{Sr}_{0.18}\text{Ti}_{1.02}\text{O}_{3.6}\text{Si}_{0.17}$
Substrate	∞	$\text{Si}_{1.00}$

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