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X-ray fluorescence material analysis initiated by high energy proton beams

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Abstract. The work presents short characteristics of X-ray fluorescence method for the material element composite diagnostics in conditions of characteristic fluorescence excitation by hard X-ray beams and high energy proton beams (PIXE). There are discussed comparative data of X-ray and ion beams excitation. Specific attention is devoted to X-ray exciting beam total reflection method (TXRF) and its adaptation to the ion beam excitation by the planar X-ray waveguide-resonator application. It is shown that the modified PIXE method allows to analyze the element composition of thin surface layer and is very effective for the light element diagnostics in it.

1. Introduction

Conventional analysis of material element composition is usually executed by use of X-ray fluorescence (XRF) method in conditions of high energy X-ray beams [1–3] or electron microbeams excitation [4, 5]. The excitation by X-ray beam application is the most simple and cheap procedure for the element concentration determinations. Standard XRF element diagnostics has at its disposal two different experimental methods based on the energy dispersion principle [6] and on the conception of wavelength dispersion [7].

First method is characterized by high rapidly, multielementness and application simplicity but demonstrates poor resolution. Second one shows a very beautiful spectral resolution but it demands a very long exposition and is characterized by one element registration possibility. In the last time, the specific branch of XRF spectrometry – the X-ray fluorescence analysis in conditions of the total external reflection of the exciting radiation flux (TXRF) takes on wide propagation [8]. Fundamental feature of the method is the fact of its realization in the total external reflection geometry. In conditions of this geometry the surface material layer with thickness 3–5 nm is excited and X-ray fluorescence yield registered by radiation detector characterizes atoms filling this layer, only. In the result, the TXRF spectrometric method demonstrates a very low background deposit in the fluorescence yield spectrum and is free from the matrix influence [9]. At the same time, TXRF spectrometry as well as any X-ray fluorescence analysis oriented on the fluorescence yield excitation by hard X-ray radiation, electron beams and gamma radiation shows some difficulties at the light element diagnostics in materials.

It is illustrated by figure 1(a), which presents Kα and Lα characteristic fluorescence excitation cross-sections for different elements in conditions of MoKα radiation flux application. YKα and AlKα

cross-section magnitudes comparison shows that the efficiency excitation of yttrium fluorescence yield is higher as the aluminum one on four orders. Some difficulties of a light elements diagnostics in materials by X-ray fluorescence analysis application can be achieved by use of the proton (particle) induced X-ray emission (PIXE) method [10, 11].

PIXE method bears some similarity to the electron excitation of X-ray fluorescence yield but it is characterized by small value of the bremsstrahlung photon intensity yield. In the result, PIXE measurements are distinguished by lower levels of the background intensity in comparison with the electron beam excitation of X-ray fluorescence. But the special feature of the PIXE spectrometry is high cross-section of the light elements X-ray fluorescence excitation. This feature is illustrated by figure 1(b) [12]. In comparison with data discussed early we can find that magnitudes of X-ray fluorescence excitation cross-section for $AlK\alpha$ and $YK\alpha$ lines in conditions of the proton beam ($E_0 = 1$ MeV) application are differed on three orders in favor of Al. So, PIXE spectrometry can be considered as the most preferable analytical nondestructive base for the light element diagnostics in materials. At the same time, it is clear that PIXE measurements characterize the element composition of the material layer, which thickness is defines by the ion beam penetration depth. Moreover, PIXE spectrometry is not free from matrix effect and every lines magnitudes in the fluorescence yield spectrum are defined by absorption factors featured for studied material.

The matrix effect overcoming is not simple task. At the same time, the overcoming of the absorption factor influence determining the depth layer forming of X-ray fluorescence yield is possible by including into the PIXE measurement scheme a new device of X-ray nanophotonics – planar X-ray waveguide-resonator [13] with specific design.
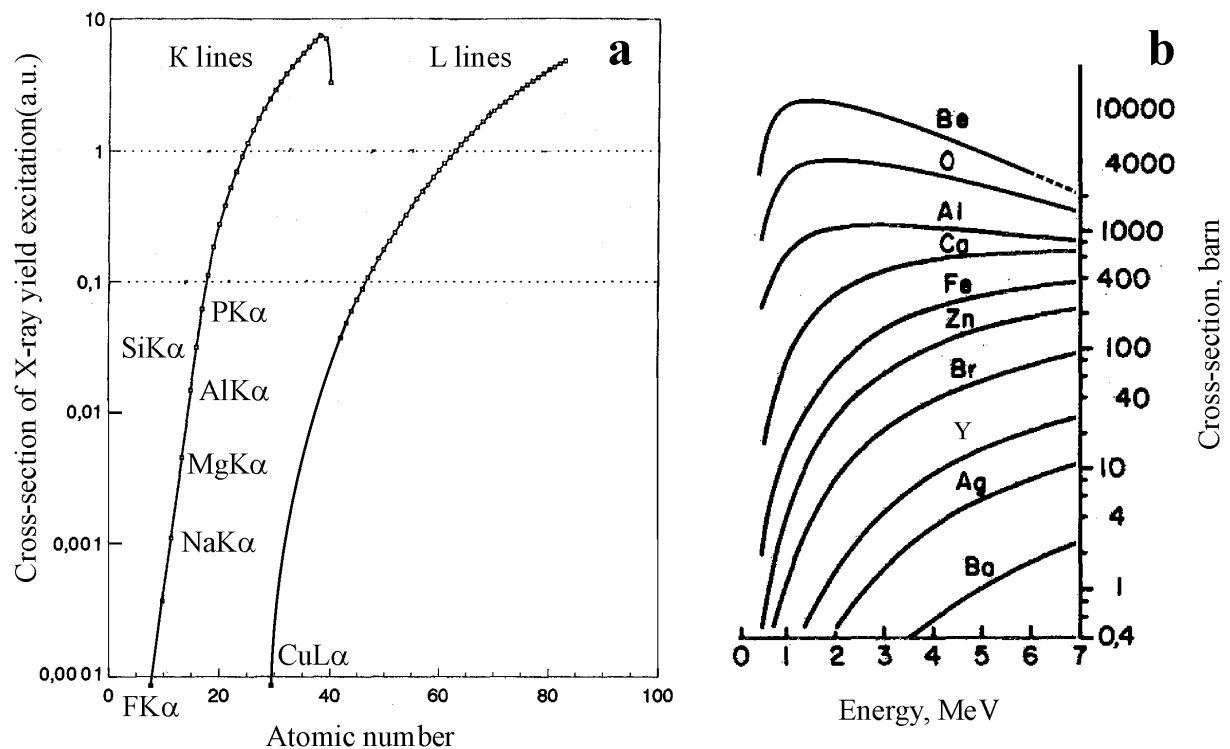

Figure 1. Cross-section functions of the X-ray fluorescence excitation by $MoK\alpha$ radiation flux **(a)** and proton beam in the energy interval 0–7 MeV [12] **(b)** for different atoms in materials.

2. Ion beam experimental facility

Experimental investigations with application of ion beams were executed by use of Sokol-3 ion beam analytical complex [14]. Figure 2(a) shows experimental vacuum chamber of the complex with set of detector and registration equipment. The chamber equipped by digital goniometer with target holder,

the double detector system for scattering ions registration and X-ray detector. Target holder has the changeable architecture and can be equipped by the planar X-ray waveguide-resonator (PXWR) with specific design (figure 2(b)). This device use allows to modify the PIXE measurement procedure.
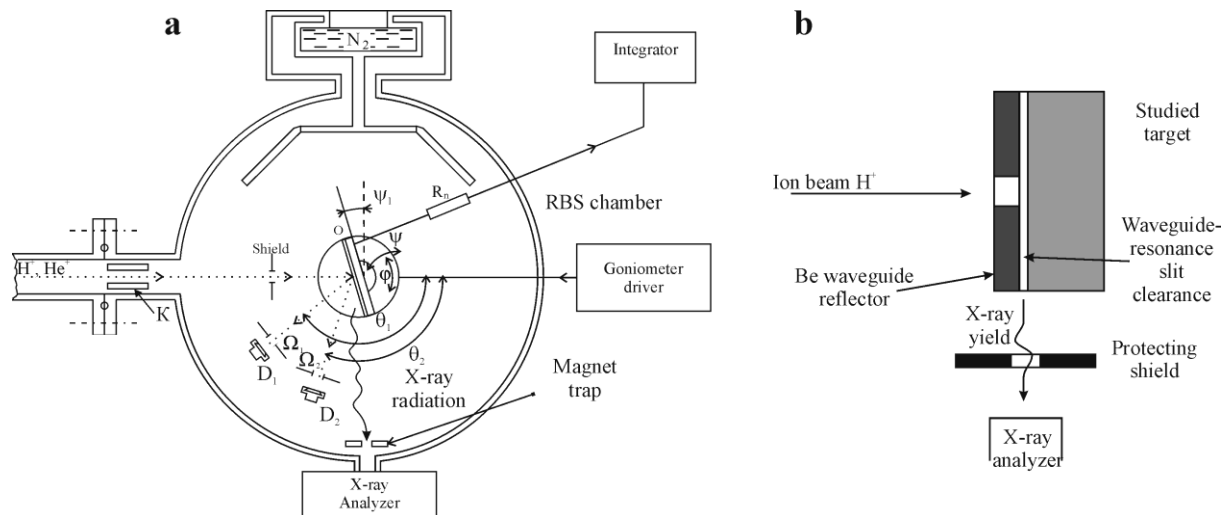

Figure 2. Scheme of Sokol-3 experimental chamber for Rutherford backscattering and PIXE experimental study of materials **(a)**. Specific peculiarity of the chamber is existence of two channels for parallel RBS spectra registration together with PIXE measurements in the same experimental session. Scheme of PIXE experimental modification for element analysis of thin surface layer of studied object **(b)**.

The idea of PXWR building is connected with discovery of new mechanism propagation of X-ray characterictical beams featured for the planar extended nanosize slit clearance [15]. Our experimental investigations showed that the PXWR with specific construction can be used with success for element composition study of the thin surface material layer in frame of PIXE measurements. Ion beam propagates into the studied target through hole in the Be polished reflector placed on some distance from the target surface. Distance between of this surface and Be plate is defined by thickness of Ti strips deposited on edges of the plate. Thickness of these strips must not exceed of half coherence length of the characteristic radiation peculiar for elements expecting in the surface material layer. Usually, this distance is selected in the interval 100–150 nm. In this case the slit clearance between the target surface and the Be plate will work as the waveguide-resonator for majority of the nature atoms characteristic radiation.

Ion beam excites target atoms X-ray fluorescence yield in a wide angular range. At the same time, the waveguide-resonance slit clearance selects the fluorescence radiation, which hits into the clearance under total external reflection angles for Be reflector, only. Flux of this radiation will correspond to fluorescence yield from the target surface layer with thickness 3–5 nm. This flux transports by the PXWR formed by Be plate and target surface and registrates by X-ray detector. In the reality, the measurements in the modified geometry can be presented as the new methodical procedure – TXRF in conditions of X-ray fluorescence at the proton beam excitation (TXRF-PE).

3. Experimental results

The surface element diagnostic possibilities of the new experimental method can be illustrated by investigation of old Soviet coin minted in 1925. It has been known that the coin was manufactured from copper alloy with silver coating. Spectrum of RBS H^+ ions on the coin presented on insertion of Figure 3 shows that the coin volume is characterized by $Cu_{0.9}Si_{0.1}$ composition. The coin coating has the thickness 170 nm and is characterized by average composition $Ag_{0.95}Fe_{0.03}Cu_{0.02}$. The diffusion layer between coating and the target volume is near 10 nm. Rutherford backscattering results are

limited by host element diagnostics owing to its low sensitivity [16]. Trace element analysis can be executed by PIXE investigation [17]. It is illustrated by figure 3(b).
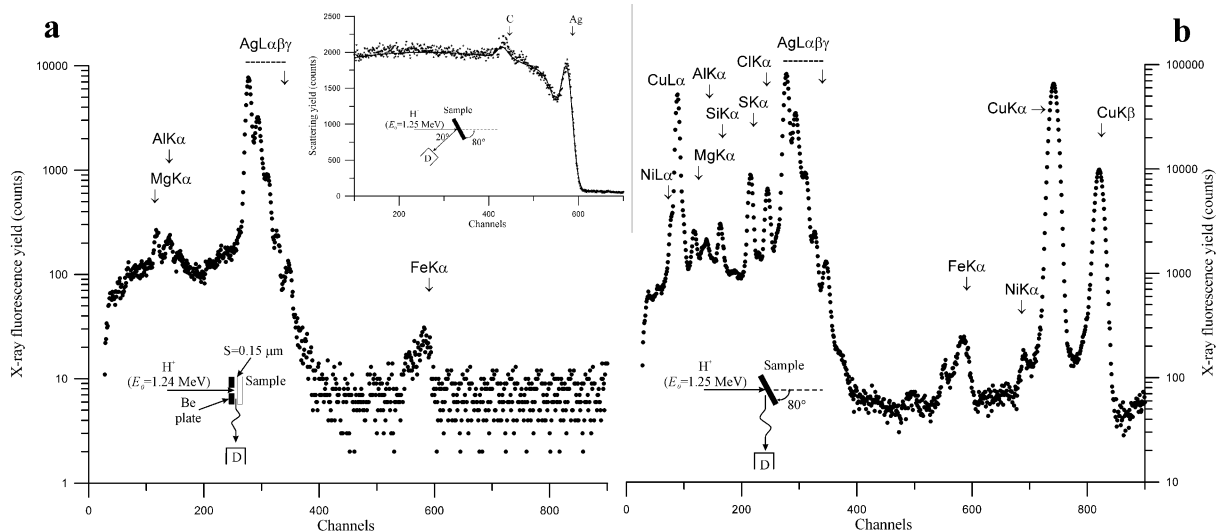

Figure 3. X-ray fluorescence spectra collected for copper coin with silver coating in conditions of conventional PIXE geometry **(b)** and modified geometry including application of the planar X-ray waveguide-resonator with specific design **(a)**. Inserts show experimental geometries of X-ray fluorescence collection and RBS H$^+$ (E$_0$ = 1.25 MeV) spectrum of the target. Arrows on fluorescence spectra show energy positions of X-ray characteristic lines and on RBS spectrum of ion scattering energies on nuclears of target surface atoms. Energy step for X-ray fluorescence spectra 10.5 eV/channel, for RBS – 1.9 keV/channel..

X-ray fluorescence spectrum presented in the figure 3(b) demonstrates CuLα, AgLα,β,γ and CuKα,β high intensity lines and set of low intensity fluorescence peaks. This spectrum was collected in the conventional PIXE geometry (see insertion in the figure 3(a)). It shows Mg, Al, S, Cl, Fe and Ni atoms presence in the target. But it is not clear contaminations whereabouts (in volume or in the target coating). The answer on this question can be received by use of the modified PIXE measurements proposing the waveguide-resonator application.

Figure 3(a) shows X-ray fluorescence spectrum of the coin in the modified geometry. The spectrum demonstrates sole high intensity composite peak AgLα,β,γ and three small intensity lines – MgKα, AlKα and FeKα. Because of the modified geometry ensures registration of X-ray characteristic fluorescence yield from the target surface layer with thickness 3–5 nm we can assert that Al, Mg and Fe atoms are contaminations for Ag coating. Quantitative determination of its content in the coating structure is not simple task owing to matrix effect influence. Quality evaluation of its content can be carried out on base of its fluorescence excitation cross-section comparison (figure 2(b)) with use data about radiation absorption in the window of X-ray detector [18]. This evaluation shows that Al, Mg and Fe atoms content in the coating structure are not exceeded 0.01% at. Integral intensity of the spectrum collected in the modified PIXE geometry is more smaller in comparison of one in case of the conventional geometry application. It is connected with very small material volume forming the fluorescence yield registered by X-ray detector. Decreasing of this volume leads to sharp reduction of the spectrum background deposit. This effect is demonstrated by figure 4.

Figure 4 presents RBS spectrum and PIXE spectra collected in conventional and modified geometries for multielement geological sample having great content of light elements. RBS investigations allow to define a principle composition of the target. But the correlation between P, Al and Si atomic concentrations from Rutherford backscattering investigations remains unelusidate. TXRF measurements carried out with PXWR application [19] added to RBS data allowed to get the material element composition as Na$_3$Zr$_{1.3}$Si$_{1.9}$Al$_{0.1}$P$_{1.0}$O$_{12}$C$_2$. At the same time, PIXE method sensitivity

is higher in composition with TXRF one in case of light element diagnostics. Figure 4 shows high sensitivity of PIXE method for verification of this elements. Comparison of X-ray fluorescence spectra collected in conventional and modified geometries demonstrates sharp decreasing of the background deposit in case of the waveguide-resonator application at the radiation yield registration. The background deposit radiation is a very important characteristics of that the new modified PIXE method because of this effect allows to expect on the contamination detection levels reduction at it use in the analytical practice.
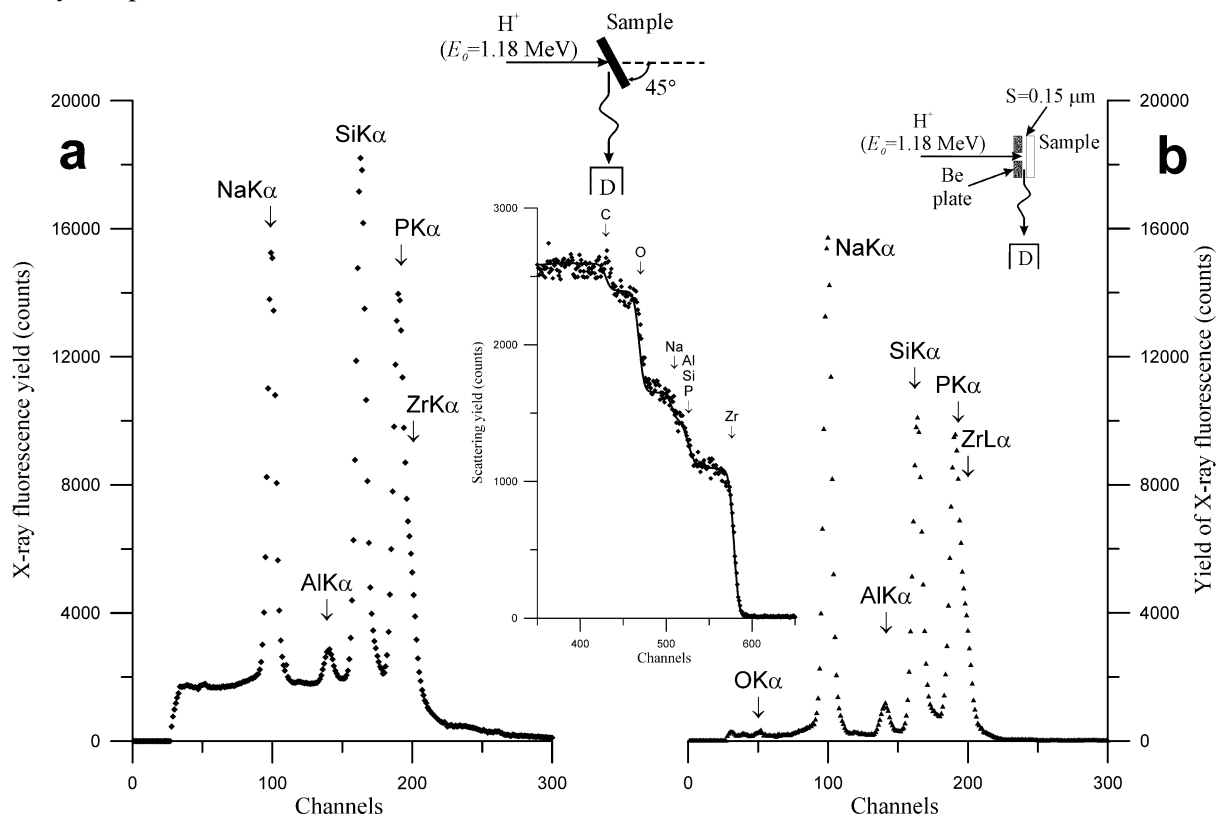

Figure 4. X-ray fluorescence spectra, collected in the conventional PIXE geometry **(a)**, and in the PIXE geometry modified by the waveguide-resonator application **(b)**. Inserts show geometries of the fluorescence spectra collection and RBS H^+ (E_0=1.18 MeV) ions spectrum. Arrows on fluorescence spectra point energy positions of X-ray characteristical lines and on RBS spectrum of ion scattering energies on nuclears of target surface atoms. Energy step for X-ray fluorescence spectra 10.5 eV/channel, for RBS – 1.9 keV/channel.

4. Conclusion

The work presents short description of experimental methods for the material element analysis XRF, TXRF and PIXE. On base of methods hybridization executed by PXWR including into the PIXE experimental scheme the new analytical method of element diagnostic for material surface layer was elaborated. Its application for real material objects showed that it is very attractive for light element analysis of thin film surface layer.

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