STATUS OF X-RAY FLUORESCENCE ELEMENTAL ANALYSIS AT VEPP-3

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The design of a synchrotron radiation X-ray fluorescence analysis (SRXFA) station installed at the VEPP-3 is described, and the basic parameters of the station are given. A double-crystal monochromator offers the possibility to work in the 4–40 keV range of excitation energies. X-ray optic elements for primary and secondary monochromatization and radiation focusing are made, by an original technology, from formed pyrolithic graphite with a curvature radius of 240–5 mm. Using a scanning system, we have obtained the element maps of geological and biological objects at concentrations up to 1 ppm and spatial resolution up to 30 μm. Using the dispersion filters makes it possible to perform analysis at an element content less than 10 ppb. Our analysis is exemplified by the case with complete external reflection, and some other experimental results are given as well.

1. Introduction

A modification of the X-ray fluorescence analysis (XFA) station which is to work using the synchrotron radiation (SR) beam from the VEPP-3 storage ring was put into operation in October 1987. The station is intended for nondistorting analysis of materials in the 4–40 keV range of excitation energies, and this allows one to identify (in K-series) the elements of the group including Cl, K and Ca to that including Ba, La and Ce.

A sample is excited by the monochromatized or white SR beam produced by a wiggler-magnet installed at the storage ring VEPP-3 (2 GeV, 20 kG, 100–200 mA). The basic measurement regimes are:

– general analysis of the elemental composition (sample mass 10^{-4}–1 g, exposure time 10^{2}–10^{3} s, characteristic values of the detection threshold 10^{-7} g/g);

– scanning across a certain part of the sample with simultaneous construction of a two-coordinate x–y map of the given elements (up to seven elements simultaneously, spatial scanning step 10 μm, measurement time per point 1–5 s, detection limit 10^{-5}–10^{-6} g/g, scanning field up to 20 × 20 mm);

– analysis of the residual amounts of the given elements (1–4 elements simultaneously) with the help of a dispersion band filter made from pyrolithic graphite (2×10^{-9} g/g detection limit for the Ru–Ag group, exposure time $(1–3) \times 10^{3}$ s);

– analysis of semiconductor plates in the complete-external-reflection regime.

2. Experimental equipment

The XFA station comprises the following basic devices (see fig. 1): a double-crystal exhausted monochro-

mator, a chamber for samples, an X–Y scanner, a semiconductor Si(Li) detector, a cylindrical dispersion band filter ("barrel"), a unit for analysis of semiconductor plates in the grazing-incidence regime, mechanisms to shift the monochromator components and the experimental chamber which are driven by stepping motors, and a site for an experimentalist; the latter covers a computer, an alphanumeric terminal and a set of electronic CAMAC modules providing the operation of all devices of the station.

2.1. Monochromator

The monochromator design permits both single- and double-crystal schemes of work. The construction is based on four mechanisms (produced by Microcontrole): two rotation units of the BG-50 type, where crystals are
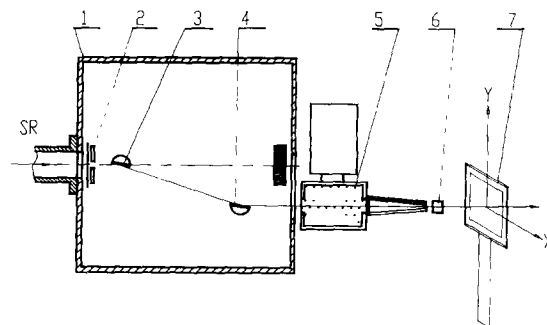

Fig. 1. Schematic diagram of the station for XFA on the storage ring VEPP-3: (1) vacuum volume, (2) beam position control, (3) formed graphite crystal, (4) flat graphite crystal, (5) ionization chamber, (6) collimator, (7) sample.
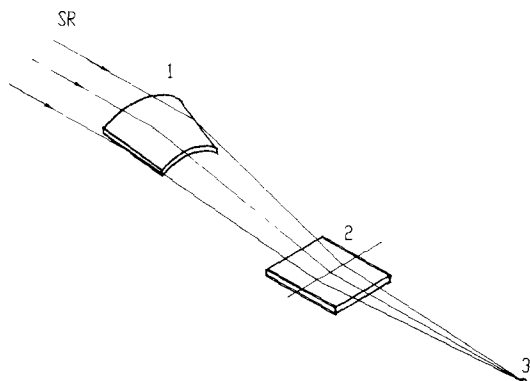
Fig. 2. Scheme of the monochromator: (1) conical graphite crystal, (2) flat graphite crystal, (3) sample.

fixed, and two translators. A horizontal translator shifts the first crystal and serves to vary the energy. A vertical translator (4.5 mm run) displaces the second crystal in order to change the position of the monochromatized SR beam on a sample. As crystal-monochromators we used flat and curved samples of pyrolithic graphite. A flat quasicrystal of pyrolithic graphite is $50 \times 50 \times 3$ mm^3 in size, the angular mosaic spread is $50'$ and the reflection factor is 20%. In the scheme with focusing along the horizontal axis we used a set of cylindrical quasicrystals from formed 40×40 mm pyrographite with fixed curvature radii.

All the monochromator elements are positioned in a $0.5 \times 0.5 \times 0.5$ m^3 vacuum volume under a working pressure of 5×10^{-2} Torr. The energy is varied and the monochromatization scheme (single- or double-crystal) is chosen by setting the Microcontrole mechanisms in a proper position using a service program.

2.2. Chamber for analysis

The chamber body and the collimators are made from a composite material on the basis of tungsten
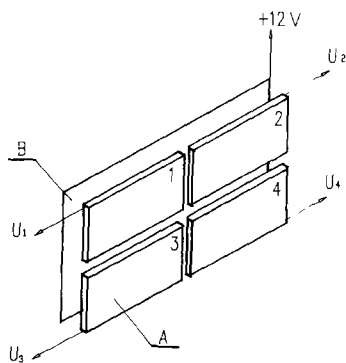

Fig. 3. Quadrupole slit or SR beam position control: (A) tantalum plate, (B) beryllium foil.

(Elconite). In the chamber we placed the scanner or, instead of it, a unit for automatic replacement of eight samples (positioner). In case of general analysis, the maximum diameter of a sample can be 30 mm.

2.3. SR beam position control

SR beam position control is carried out by means of a quadrupole slit mounted in front of the first crystal. The slit (see fig. 3) consists of four tantalum plates and a beryllium foil in front of them, with a small positive potential applied to it ($+12$ V). All the elements are isolated. The device operates under prevacuum conditions ($10-10^{-2}$ Torr). The voltages U_1-U_4 at the Ta plates are sufficiently high (0.2–2 V) and there is no need for an amplifier. These are measured by means of a commuting analog–digital converter and are introduced into a computer. The vertical (δ_v) and horizontal (δ_h) beam deflections from the geometrical centre of the slit are measured in arbitrary %:

$$\delta_v = \frac{(U_1 + U_2) - (U_3 + U_4)}{U_1 + U_2 + U_3 + U_4},$$

$$\delta_h = \frac{(U_2 + U_4) - (U_1 + U_3)}{U_1 + U_2 + U_3 + U_4}.$$

The quantities δ_v and δ_h thus found do not practically depend on the residual pressure in the vacuum volume of the monochromator, although the values of $U_1 - U_4$ can change considerably during its pumping.

The information obtained on the vertical shift of the SR beam allows one to rapidly set the monochromator in the median plane ($\delta_v = 0$), where the coefficient of linear radiation polarization is maximum. This provides the best signal-to-background ratio in the fluorescence spectrum. Besides, the achieved stability of the polarization coefficient improves the reproducibility of the results in quantitative analysis.

3. Scanning microanalysis

Micro-XFA using synchrotron radiation has some significant advantages over a technique so broadly used as electron microprobing [1–3]. Among the advantages being of value for geological samples, there are the possibility of analysis of the elemental mapping at a considerably lower level of concentration (100–1 ppm and lower), the possibility of identification of heavy elements using K-series and, especially, the possibility of selective excitation of the elements in a complex matrix.

To analyse the elemental composition of the microsection metallographic specimens of rocks, ores and minerals, the authors have designed and tested a device comprising a mechanical scanner and a semiconductor
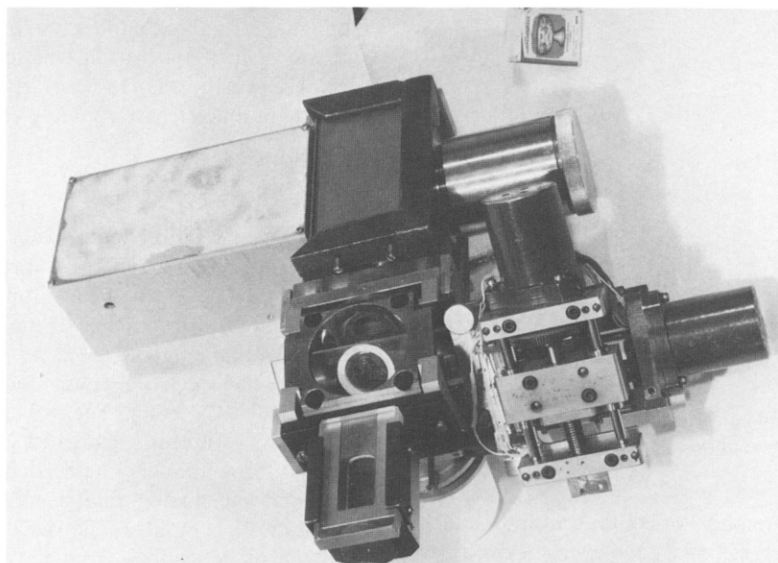
Fig. 4. General view of the chamber with the sample, the scanner and the ionization chamber.

detector. To achieve a maximum flux of quanta, a single-crystal scheme of monochromatization was used.

The air-filled sample chamber was made from tungsten. In the chamber there is a scanner allowing a shift, with a 10 μm step, of the sample in two mutually perpendicular directions within the 20×20 mm^2 area. The scanner is motor-driven, and the two stepping motors for this purpose are computer-controlled.

During the measurements the following signals were monitored: (a) a signal from the ionization chamber placed in the monochromatized beam in front of the last collimator, (b) the area of the Compton scattering peak due to the exciting radiation, and (c) the area of the fluorescent peak from a metallic foil located at the back of the sample being examined (substrate technique). The general view of the chamber with the sample, the scanner and the ionization chamber is shown in fig. 4.

As collimators we have employed conical holes drilled in a 1 mm thick lead sheet placed on a hard metallic plate. The effective diameter of such a collimator depends on the working range of energies and was determined experimentally with respect to the broadening of the image lines when scanning a thin nickel grid.

The necessity to achieve a peak of the element under study within the rather small statistical error leads to the dependence of the spatial resolution on the concentration of the element, the exciting beam intensity and on the exposure time at a point. Without focusing X-ray optics, the spatial resolution was about 60 μm in the monochromatic beam and about 30 μm in the white SR beam for an exposure time of 1 s/point. The minimum detectable concentration of the elements

ranging from Fe to Sr was 10 ppm at a measurement time of 1–3 s/point (with monochromatized excitation).

To study the element mapping in minerals, we have prepared thin (0.30–0.5 mm) planar and parallel plates of up to 1 in. diameter. During the scanning we managed to identify simultaneously eight elements with a Si(Li) semiconductor detector. Fig. 5 illustrates the Fe and Sr maps in the rock section with garnet grains. The circular regions of high concentration of Sr are the result of segregation as the garnet crystals grow. The Sr concentration in the map varies from 10 to 300 ppm.

This technique has also been applied successfully to some biological problems, for example to the measurement of images of lymphonodes with X-ray contrast substances on the basis of a gold-containing colloid introduced into them [4]. In addition, first pictures of artificial fluidized inclusions in minerals have been obtained *; this work and some others in this series are planned to continue after modernization of the monochromatization system.

4. Graphite-based X-ray optics

The elements for X-ray monochromatization and focusing were manufactured by A.A. Antonov and I.G. Grigoryeva ** by their original technology [5]. A set of

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* This work is being carried out by Yu.M. Ishkov and his colleagues (Institute of Geology, Ulan-Ude, USSR).
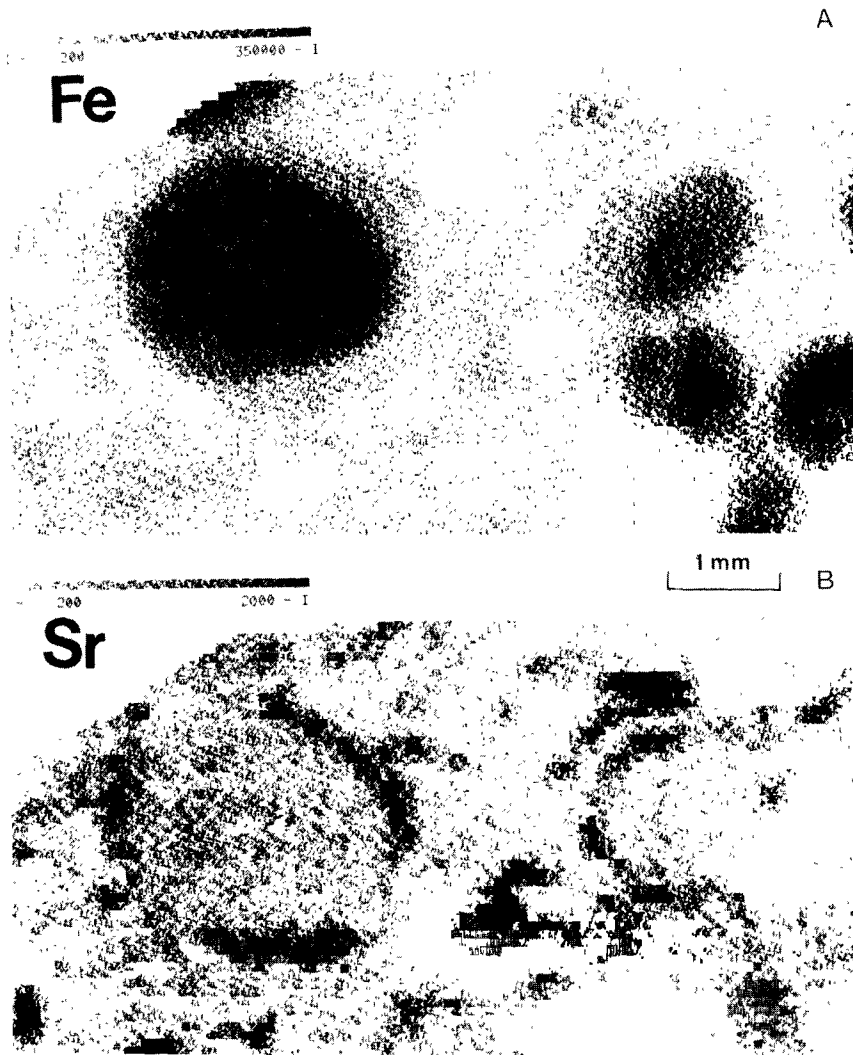** Institute of Graphite-Based Materials of Construction, Moscow, USSR.

Fig. 5. Two-dimensional chart of iron (A) and strontium (B) distribution in the microsection metallographic specimen of a rock. The regions with high content of iron are the garnet grains; 100×60 points, measurement time 1 5 s/point, scanning step 80×80 μm^2, monochromatic excitation, $E = 20$ keV.

highly bent crystal-monochromators has been manufactured from flat ones of ZYB type with a FWHM mosaic spread ranging from 50' to 60'. Special chemical treatment, preserving the initial mosaic spread and perfect crystalline structure, transfers a crystal-monochromator into a flexible state. The flexible crystal is pressed onto a substrate and becomes a replica of the required shape. This method does not impose any limitations on the shape of the exposal area of monochromators.

Two types of monochromators were tested, using the SR beam from the VEPP-3 storage ring, in the following devices:
- short-focus wide-band cylindrical and conical mono-chromators (radii 5–240 mm) for the SR energy range from 4 to 40 keV (fig. 6);

- a dispersion filter of secondary (fluorescent) radiation for XFA (the cylinder is made from four segments with 12.5 mm inner radius and 30 mm length).

5. Secondary monochromatization

The sensitivity of XFA with a semiconductor detector involved can be raised substantially (by one or two orders of magnitude) in the cases when only one or a few elements closely spaced in the periodic system should be identified and the X-ray fluorescence excitation source has a sufficiently large reserve in intensity. The sensitivity can be improved by placing a dispersion filter between the sample under measurement and a
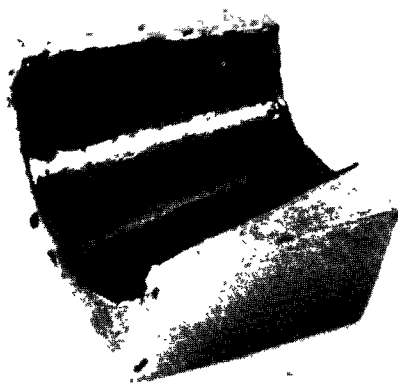
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Fig. 6. General view of the conical graphite monochromator (R_1 = 20 mm, R_2 = 12 mm).
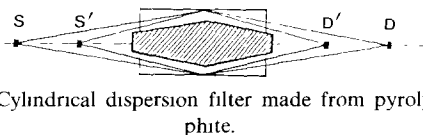

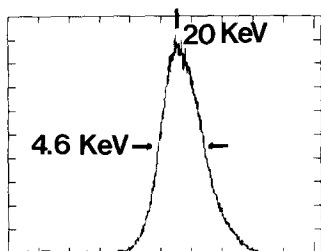Fig. 7. Cylindrical dispersion filter made from pyrolytic graphite.

Fig. 8 Transmission band of a dispersion filter (measured using the white SR beam from the storage ring VEPP-3).

detector (see fig. 7). In this case, the detector is made free from a counting of intense spectral lines: elastic and Compton scattering of the exciting scattering, Fe lines, etc.

The authors have found the detection limits for the group of light platinoids (Ru, Rh and Pd) and silver in samples of ores and technological products, using the SRXFA technique by means of a cylindrical dispersion filter made from formed pyrolithic graphite. To find the detection limits for the indicated group of elements, the standards VT-1, KM-1, KN-1 and KhO-1 were analysed at an excitation energy ranging from 27 to 29 keV. The transmission band of a filter was 20 ± 2.3 keV (see fig. 8). One of the obtained spectra can be seen in fig. 9.

It is worth noting that the SR beam generated by the nonsuperconducting wiggler-magnet of the VEPP-3
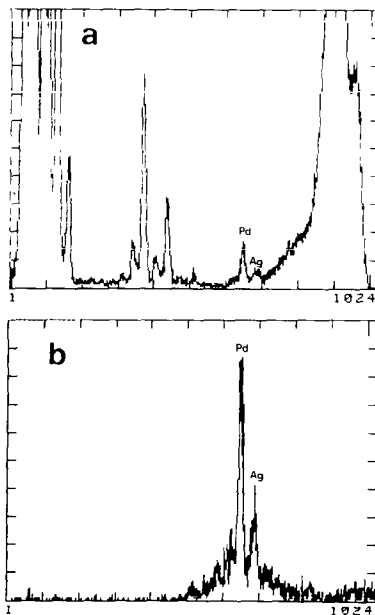

Fig. 9. Spectra of a rock reference sample containing 6.4 ppm of palladium and 2.6 ppm of silver. (a) direct measurement using SSD, (b) using the dispersion filter.

storage ring and monochromatized by a flat crystal of pyrolithic graphite provided a counting rate of the detector from 10 to 100 Hz for work in the 28–30 keV range of excitation energies. And, hence, the metrological characteristics were defined at small sets of statistical data (15 000–100 000 pulses per spectrum). The measured area of the fluorescent peaks of light platinoids was up to 4% of the total integral of the spectrum at a concentration of the element of 1 ppm. The signal-to-background ratio for the K_α Pd line in VT-1 (concentration 6.4 ppm) was 50–60.

For the group of elements under consideration, the detection limits are 16.5 ppb for a spectrum with a 10^5 pulse integral and 2.7 ppb for a total integral of 3.6×10^6 pulses.

6. Grazing-incidence analysis

This variant of a highly sensitive SRXFA [6] is used to control the concentration of the elements after ion implantation into silicon semiconductor plates.

As an example, we present the results obtained for As-implanted plates *. During the measurement process, the signal/background and signal/Compton ratios

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* The samples were presented by N.V Peretolchin, Institute of Semiconductor Physics, Moscow, USSR.

Table 1
The results of SRXFA of As-implanted silicon plates; the implanted dose is 10^{-3} C/cm^2

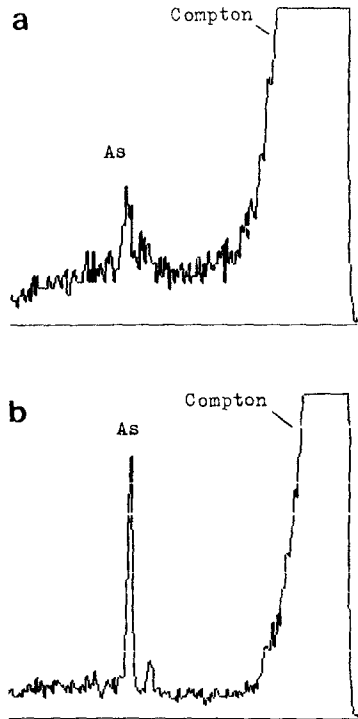| Incidence angle [deg]	Signal/Compton ratio [rel. units]	Signal/background ratio	Detection limit for 10^3 s [$\mu C/cm^2$]
45	10.4	0.361	113 4
5	28.9	0.72	43.8
0.5	100	5.28	4 15

Fig. 10. The spectra of an As-implanted silicon plate; incidence angle (a) 45°, (b) 0.5°

were determined for the As line while varying the incidence angle of exciting radiation from 45° to 0.5° (see fig. 10). The results of the measurements are listed in table 1. The ultimate detection dose of the implanted As is 4.15×10^{-6} C/cm^2 for a measurement time of 10^3 s and an incidence angle of 0.5°. Further decrease of the incidence angle turned out to be inefficient in our case because of the angular spread of the exciting radiation which is due to the mosaic structure of the pyrographite crystal-monochromator.

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