

## REVIEW OF X-RAY FLUORESCENT ANALYSIS USING SYNCHROTRON RADIATION

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The current status of research in X-ray fluorescent analysis using synchrotron radiation (SRXFA) is reviewed. The main schemes of analysis and the background components are considered. The methods of reducing the background, which are based on the use of the specific features of synchrotron radiation, are discussed.

The requirements for the elements of the SRXFA apparatus including the source of synchrotron radiation, the monochromator, a chamber for the sample, scanner and the detector are formulated. The engineering solutions which can be used when designing these elements are suggested. The main results obtained by the SRXFA method and the possibilities for their further improvement are discussed.

### 1. Introduction

In the last decade, work on the development of the technique of X-ray fluorescent element analysis using synchrotron radiation (SRXFA) has been carried out using various sources of SR. The publications available can be grouped into two categories: a comparatively small amount of pioneering experimental work performed prior to 1980 at the sources CEA, SPEAR, VEPP-3 [1–4], and a considerably larger, and rapidly growing, amount of current work dealing with improvements of the SRXFA technique and its numerous applications.

A rapid growth of the number of experimental groups involved in work with SRXFA is due both to the putting into operation of new storage rings, including dedicated SR sources (SRS, Photon Factory, NSLS) and to the modernization of the already existing ones by installing on them wiggler magnets, which allow a substantial increase of the intensity and the hardness of the SR beams extracted.

Table 1 lists eight storage rings which are being employed (or have been employed) in SRXFA studies.

Among the first work on SRXFA the experiment of Sparks et al. [3], which was made using the monochromatic SR beam from the SPEAR storage ring in 1976, is

Table 1  
First publications devoted to SRXFA

SR sources	Year of publication	Authors
CEA (Cambridge, USA)	1972	P. Horowitz, J. Howell [1].
SPEAR (Stanford, USA)	1975	C. Sparks, J. Hastings [2].
VEPP-3 (Novosibirsk, USSR)	1977	V. Ilyin, G. Kazakevich, G. Kulipanov, L. Mazalov, A. Matyushin, A. Skrinsky, M. Sheromov [4].
VEPP-4 (Novosibirsk, USSR)	1983	V. Baryshev, Y. Kolmogorov, G. Kulipanov, A. Skrinsky [7].
SRS (Daresbury, England)	1983	D. Bowen, S. Davies [8].
DORIS (Hamburg, FRG)	1983	A. Knoechel, W. Petersen, G. Tolkiehn [9].
CHES (Cornell, USA)	1983	A. Hanson, H. Kraner, K. Jores, B. Gordon, R. Mills, J. Chen [10].
Photon Factory (Tsukuba, Japan)	1985	A. Iida, K. Sakurai, T. Matsushita [11].

apparently, the most important and well known. Great possibilities for the new method were demonstrated.

In 1976 SRXFA studies were started at Novosibirsk on the SR beam from the VEPP-3 bending magnet in the energy range up to 15 keV [4].

In 1981/82 a number of applied and methodological studies of XFA were made including the multielement analysis of medical and geological samples in the energy range up to 50 keV with a 30 ppb detection threshold [15]; the complex analysis of samples from the copper-ore deposit "Udokan" [16] and the testing of the dispersive device intended to detect the L-series of hypothetical natural superheavy elements [17]. These studies were carried out using a 1 kW SR beam from the 20-pole superconducting wiggler-magnet ("snake") of the storage ring VEPP-3 [12–14].

With the beginning of the work using SR beams from the storage ring VEPP-4 in 1982, a permanently operating station intended for mass elemental analysis with a monochromatized excitation tunable over a broad energy range (10 to 100 keV) was arranged [7]. At present, 12 experimental groups from geological, medical and industrial institutions participate in work using this station. Among the studies performed are an analysis of Moon samples (weight ranging from 3 to 0.1 mg) which were delivered by Luna-16 and Apollo-17 [18], an analysis of the processes in the lymphatic system [20], a complex analysis on the detection of light platinoids with a sensitivity up to 10 ppb [21], and others.

Since 1983 a great variety of methodological studies on SRXFA have been made at DORIS, SRS and CHESS [8–10]. Of great interest is the work on various schemes of SR monochromatization for XFA, which has been performed at the Photon Factory [11]. There, a surface elemental analysis was also made using the XFA grazing incidence [22]. Of interest are the results on scanning microanalysis with a spatial resolution of about 10  $\mu\text{m}$ , which were obtained in Hasylab [23]. Work on XFA of light elements are in progress using the SR beam from an undulator in Tsukuba [24].

The development of the SRXFA technique in differ-

ent research centres has demonstrated that it has the following advantages:

- high sensitivity (1 ppb for wavelength-dispersive and 10 ppb for energy-dispersive XFA);
- only a small volume and weight of the sample under study is needed;
- multielemental application (from Na to the end of the Periodic Table concentrations can be measured for all elements without exception);
- nondestructive measurement procedures;
- rapid obtaining of results;
- the possibility of measuring the surface and volume distributions of elements;
- the possibility of arranging an automated elemental analysis for applied purposes (geology, industry, medicine, crime detection, etc.).

## 2. SRXFA schemes

Depending on the problem to be solved, for XFA on SR beams various schemes, distinguished by the methods of excitation and detection of fluorescent quanta, are applicable.

To measure minimum concentrations for one or a few elements in samples of comparatively large weight, it is necessary to utilize monochromatized SR with an energy near the K- (or L-) absorption edges of the elements studied. Monochromatization eliminates the background in the detection region, which is caused by the scattering of the exciting radiation on the sample.

In a local elemental analysis when the area and weight of the sample part studied is sharply decreased, the total amount of SR quanta interacting with the sample becomes limited (and these may be too low a counting rate in the detector). Under these conditions excitation by a wide-band spectrum is preferable. This is obtained from the primary beam with the help of focusing mirrors or by a focusing mirror coupled with an absorption filter, as well as by means of a white (non-monochromatized) SR beam. In this case, the

Table 2 <sup>a)</sup>

Comparison of the MDLs for different methods of excitation. A series of samples of metal absorbed chelate resins was measured. Counting time was 100 s except in conventional XFA where a 600 s counting time was used. In the continuum with absorber excitation, 280  $\mu\text{m}$  thick Al was employed. A Ge target was used as the secondary fluorescer in conventional XFA experiments.

Excitation mode	MDL (in relative concentration)			Irradiation area	MDL (in absolute amount) Zn
	Zn	Mn	Ca		
Continuum	550 ppb	410 ppb	440 ppb	$3.5 \times 10^{-3} \text{ mm}^2$	0.13 $\mu\text{g}$
Continuum with absorber	170 ppb	240 ppb	750 ppb	$2.8 \times 10^{-2} \text{ mm}^2$	0.34 $\mu\text{g}$
Monochromatic	60 ppb	70 ppb	200 ppb	$1.1 \text{ mm}^2$	4.7 $\mu\text{g}$
Conventional XFA	1.9 ppm	2.0 ppm	8.8 ppm	$3 \text{ cm}^2$	40 $\mu\text{g}$

<sup>a)</sup> After Iida et al. [11].

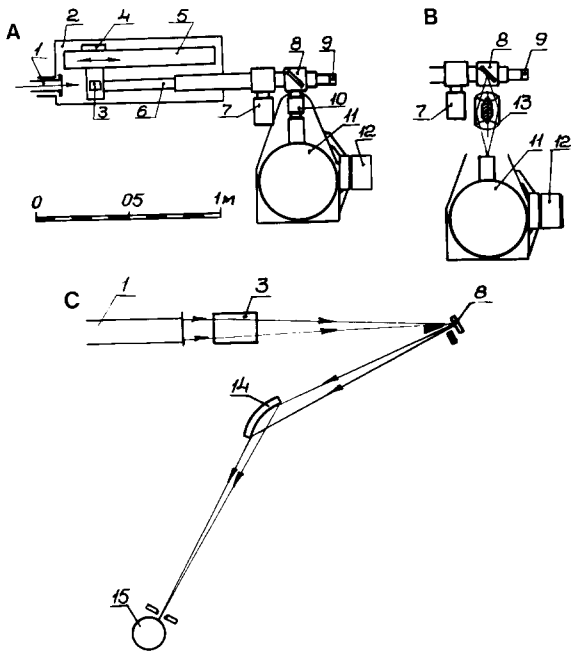


Fig. 1. Three registration schemes: (A) multielement energy-dispersive analysis [7,28]; (B) the 1-3 element analysis of higher sensitivity with the use of an axial dispersion filter made of pyrolytic graphite; (C) 1-element wavelength-dispersive analysis [17]. 1 - SR beam line, 2 - box, 3 - crystal-monochromator, 4 - stepping-motor, 5 - monochromator driver, 6 - tube, 7 - polarimeter, 8 - sample, 9 - absorber of SR beam, 10 - collimators, 11 - SSD, 12 - bending table, 13 - dispersion filter, 14 - crystal-analyser, 15 - counter.

minimum detectable concentration will be larger (weak relative sensitivity); the minimum registered amount of an element becomes less. Table 2 presents the results of the methodological studies, performed at the Photon Factory, on the optimization of monochromatization systems for SRXFA.

Three basic schemes, illustrated in fig. 1, are used for the detection of XFA spectra. The advantage of scheme A (energy-dispersive analysis) consists of the relative simplicity of the quantitative multielemental analysis and the wide range of simultaneously detectable elements. The relative sensitivity of the method is limited by the insufficient energy resolution of the SSD ( $\geq 150$  eV). This is mainly revealed in the presence of elements with interfering spectral lines, and by the slow action of the detector (usually no more than  $10^4$  Hz). As calculations [25,26] and experimental data [3,6,7,15] show, the ultimately detectable concentration of elements from the middle part of the Periodic Table is 10-30 ppb for this scheme, for a  $10^3$  s exposure. The large solid angle of detection of the SSD enables extremely high absolute sensitivity to be achieved in scheme A.

The detection limit and the measurement time in this scheme can be substantially improved by replacing the single-channel SSD by a mosaic (multichannel) one.

Scheme C (wavelength-dispersive analysis) is the combination of a focusing crystal-monochromator with a focusing crystal-analyser and allows an analysis of a particular element to be performed with higher relative sensitivity. The maximum signal-to-background ratio in scheme C is achieved at an energy resolution of the crystal-analyser close to the natural width of the X-ray emission line (about 1-3 eV). In practice, however, the

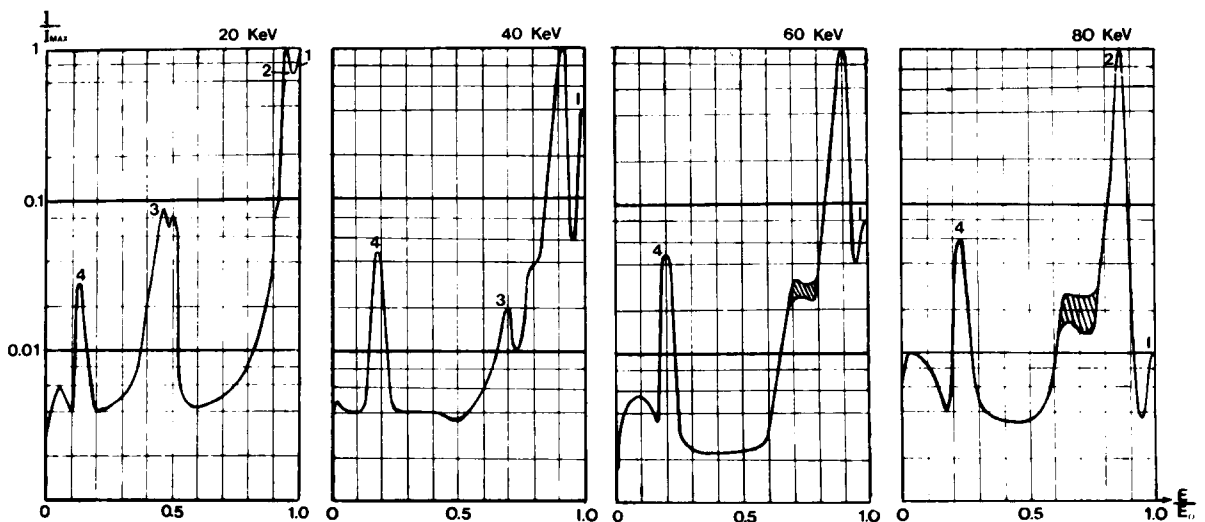


Fig. 2. Spectra of 0.5 mm thick Si-plate (VEPP-4, detector from Ge, excitation energy 20-80 keV). 1 - elastic, 2 - Compton peak, 3 - fluorescent escape peak, 4 - Compton scattering in detector.

solid angle of detection of such a narrow-band system can turn out to be too small. Taking the limited intensity of the SR source to provide an acceptable counting rate of the detector into account, the optimum resolution of the analyser can be from one to several tens of eV.

Multielemental analysis in scheme C can be realized either by scanning the analyser energy range with an appropriate increase of the total time of analysis, or by increasing the number of crystal-analysers (multichannel detection).

The advantages of the wavelength-dispersive detection scheme are completely realized on the intense SR beams from wiggler magnets. In this case, the expected sensitivity of the analysis is 1–0.1 ppb during an exposure up to  $10^4$  s [26].

In scheme B a cylindrical dispersion filter of pyrolytic graphite is placed between the sample and the SSD. The transmission band of such a filter is 2–4 keV over the 10–20 keV range of detected quanta energies. Scheme C allows the analysis of 1–3 elements to be carried out with an increased sensitivity (due to a decrease in the counting rate of the detector) and, in principle, studies with radioactive samples can be performed [27]. According to the major characteristics (detection limit, solid detection angle, number of simultaneously measured spectral lines), scheme B seen occupies the intermediate position between schemes A and C.

### 3. Basic components of the background in XFA on SR beams

The exciting radiation interaction with a sample is of a rather complicated nature, therefore, some multiple background components are added to the sample emission spectrum. With the practically infinite flux of exciting quanta, it is the spectral density of the background in the region of the lines being analysed and the counting rate of the detector that mainly determine the XFA sensitivity. In the most common case of excitation by monochromatized radiation of samples with a light matrix the background has the form of (see fig. 2):

- (1) a peak from the elastic scattering of the exciting radiation;
- (2) a peak from the Compton scattering of the same radiation (single for thin samples and multiple for thick ones);
- (3) escape peaks of detector fluorescence emission, spaced from the elastic and Compton peaks as well as from the rather intense spectral lines of the sample at the energy of the fluorescence quantum emission of the detector material (9.9 keV for Ge);
- (4) escape peaks of detected quanta, Compton-scattered in the detector at an angle of about  $180^\circ$  and

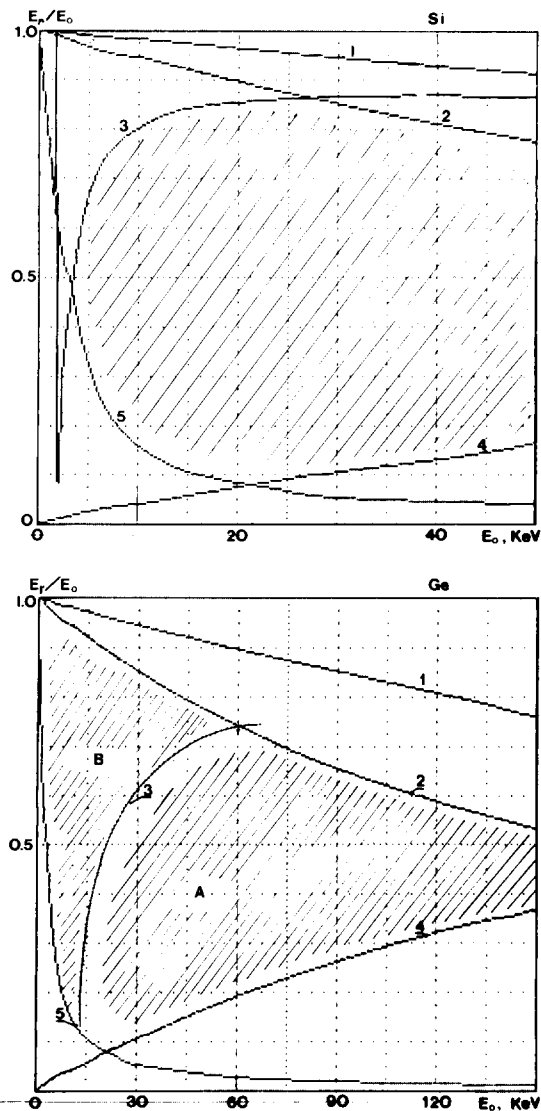


Fig. 3. Registration energy regions for Si and Ge SSD. 1 and 2 – Compton and double-Compton scattering of excitation quanta, 3 – fluorescent escape peak (for Ge SSD), 4 – Compton in a detector, 5 – absorption in SSD foil.  $E_0$  – excitation energy,  $E_r$  – energy registered.

leaving it along the shortest path; in this case, the detector registers the recoil electron alone; when these are many intense lines in the spectrum of a sample, or when the detector is of insufficient thickness, the indicated peaks form a continuous background in the low-energy region;

- (5) a plateau formed by the bremsstrahlung from photoelectrons in the sample, an incomplete charge collection in the detector as well as by the part of the secondary quanta that leave the detector.

Fig. 3 illustrates the detection regions for Ge and Si detectors in which, with the above factors taken into

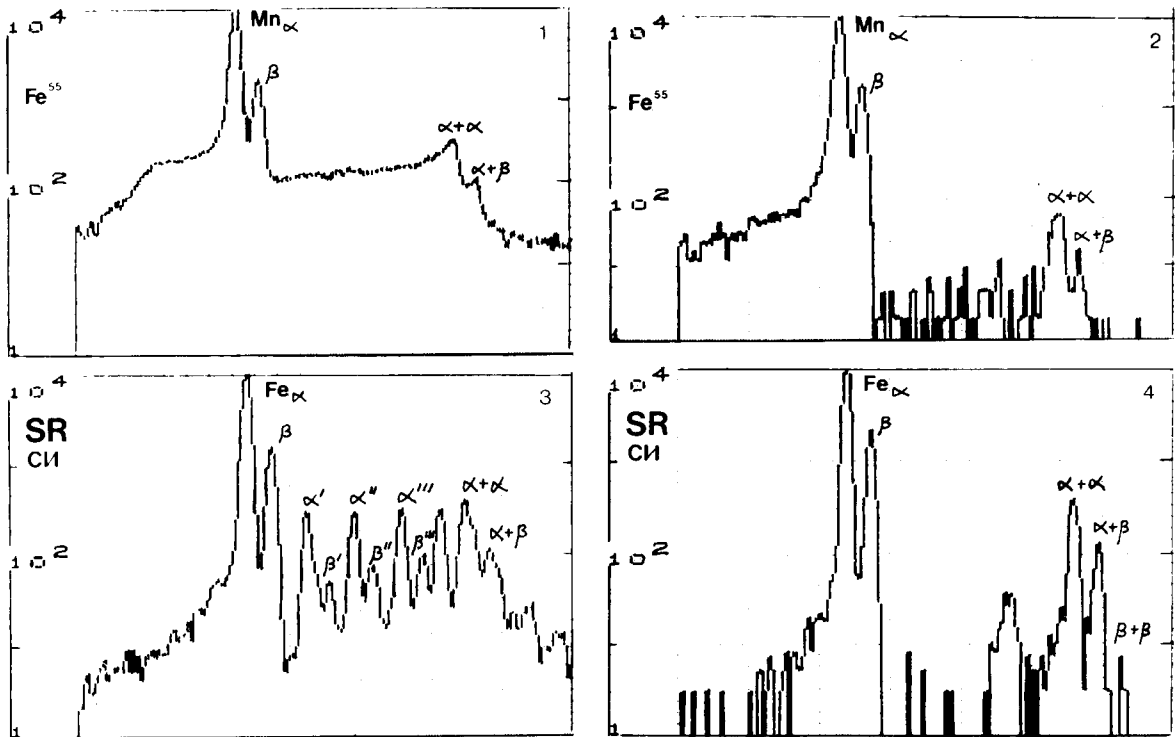


Fig. 4. Spectra of isotope  $^{55}\text{Fe}$  (1 and 2) and Fe sample with SR excitation (3 and 4). Counting rate 30 kHz, SR from VEPP-4 (2.4 – with using of the antpileup rejector). Combinatorial lines of two types are seen in the spectra: a) physical lines  $\alpha + \alpha$ ,  $\alpha + \beta$ ,  $\beta + \beta$ ; b) an electronics effect  $\alpha'$ ,  $\beta'$ ,  $\alpha''$ ,  $\beta''$ . The time constant of the amplifier is  $5 \mu\text{s}$ .

account, the lowest spectral density of the background is achieved at different excitation energy ranges.

With a limited counting rate for the detector, the “background” also comprises the high intensity spectral lines belonging to the other (not under analysis) elements. In addition, the use SR for fluorescence excitation, especially in the single bunch operation mode of the storage ring, leads to the appearance of combinatorial lines in the XFA spectra which do not exist in reality.

The increase of the SSD counting rate and the application of conventional excitation sources such as X-ray tubes, isotopes give rise to the appearance in the measured spectrum of a continuous background connected with the random superposition of electric signals in spectrometric amplifiers (see fig. 4).

Synchrotron radiation reflects the time structure of the electron beam in the storage ring. Therefore, for a single bunch operation mode of the storage ring the SR time structure is the succession of short pulses (“bursts”) of duration  $\tau$ , repeated with the period of revolution of an electron in the storage ring,  $T$ . For example,  $\tau = 0.3 \text{ ns}$  and  $T = 1.2 \mu\text{s}$  for the storage ring VEPP-4.

The pulse nature of the radiation leads to an increase of the superpositions at a given average detector counting rate and to the appearance of a discrete background

consisting of combinatorial lines of two types rather than a continuous background [7].

The first type is combinatorial lines that cannot be suppressed with electronics (pile-up rejector). The peak counting rate of the detector at the moment of SR irradiation is  $T/\tau$  times higher than the mean counting rate ( $T/\tau = 4000$  for VEPP-4). Because of this fact a probability for superposition of 2, 3 or more photons in the detector itself increases strongly. Since the irradiation time for the single SR bunch is much lower than the time for charge collection in the SSD ( $0.1 \mu\text{s}$ ), two fluorescent photons with energies  $E_1$  and  $E_2$  reaching the detector for the SR single bunch will be summed up and interpreted as a single photon of energy  $(E_1 + E_2)$ . As a result of this effect,  $k(k+1)/2$  nonexistent combinatorial lines, the intensity of which is proportional to the square of the mean counting rate of the detector will be added to an initial emission spectra containing  $k$  intense lines.

The second type comprises combinatorial lines, the appearance of which is due to the fact that upon the X-ray quantum detection in the spectrometric amplifier a long enough signal is formed ( $4\text{--}12 \mu\text{s}$ ). Since the next signal can come in a time multiple of the storage ring repetition rate, the amplitude spectrum of the superimposed pulses is discrete. The spectrum line position

depends on the selected forming time of the amplifier and also on the operation mode of the storage ring (single bunch, or multibunch mode). Combinatorial lines of this type are eliminated by an anti-pile-up rejector. The characteristic shape of the lines of both types are shown in fig. 4.

The counting rate  $f_{1,2}$  of a combinatorial line of energy ( $E_1 + E_2$ ) is:

$$f_{1,2} = f_1 f_2 / (mF), \quad (f_1, f_2 \ll F),$$

where  $f_1$  and  $f_2$  are the counting rates of real spectral lines with energy  $E_1$  and  $E_2$ , respectively;  $F$  is the electron revolution frequency in the storage ring and  $m$  is the number of electron bunches.

As the work on VEPP-4 has shown, the combinatorial lines are one of the major components of background which limits the detection threshold in multielemental analysis of samples of complex composition.

A radical measure to suppress the combinatorial lines is the application of a wavelength-dispersive detection scheme or of dispersion filters (see figs. 1B and 1C). In practice, the installation of an absorption filter between sample and detector has the same effect.

These methods narrow the range of simultaneously analysed elements. The intensity of the combinatorial lines can be reduced without narrowing the detection range by increasing the number of bunches  $m$  in the storage ring and also by applying a multichannel solid state detector.

#### 4. Methods of increasing the XFA sensitivity using SR

The use of the specific features of SR makes it possible to reduce substantially the background and, hence, to improve the sensitivity and to shorten the time of analysis.

*Selective excitation:* If the emission spectrum has peaks with logarithmical differences in intensity, excitation of some parts of a spectrum would better be done separately by varying the excitation conditions (monochromatization energy is set higher and lower than the K-absorption edge of an element of high concentration). Selective excitation requires good suppression of heavy element lines during detection of fluorescent quanta of lighter elements.

To exclude higher orders, it is more convenient in this case to monochromatize the SR by employing a mirror coupled with an absorption filter or a mirror coupled with a crystal-monochromator. In work on SR beams from wiggler magnets, the intensity of the second harmonic of the crystal-monochromator can be reduced if the magnetic field at the irradiation point is chosen so that the spectral flux of doubled-energy photons becomes rather small.

Fig. 5 illustrates the procedure for selective excita-

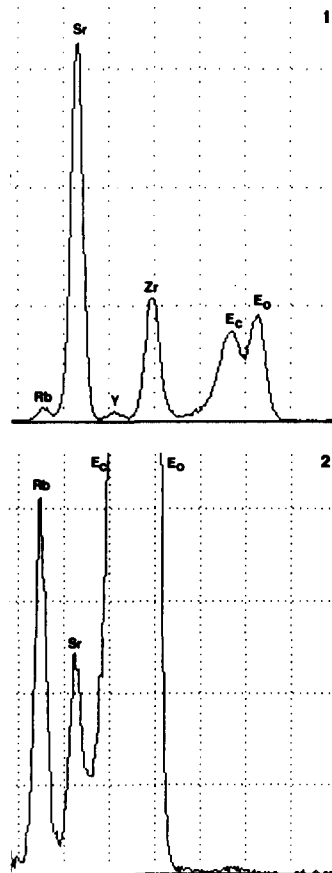


Fig. 5. Selective excitation procedure. Rb analysis in an SGD-1 standard; background lines: Sr K-series (1 shot). The analysis is provided by damping the Sr lines with an energy decrease.

tion of a standard rock sample SGD-1 with a large content of Sr for the observation of Rb. By lowering the monochromator energy the Sr K $\alpha$  line is suppressed, thereby improving the conditions for quantitative Rb analysis.

*Selective detection:* With a limited counting rate of the solid state detector the detection of certain parts of a spectrum would also be better performed separately. In the simplest case of two peaks with intensities  $I_1$  and  $I_2$  ( $I_1 \gg I_2$ ) the total time for separate peak measurements  $t(1 + I_2/I_1)$  is substantially lower than for simultaneous measurements of two peaks  $tI_1/I_2$  at a given signal/background ratio for the lower peak (i.e. with the qualities being equal).

With closely positioned peaks the effect can be even higher, since Compton scattering of intense line radiation can strongly increase the background in the weak line observation area.

Limitation of the spectrum area to be detected makes the signal/background ratio better in XFA since the background connected with an incomplete charge col-

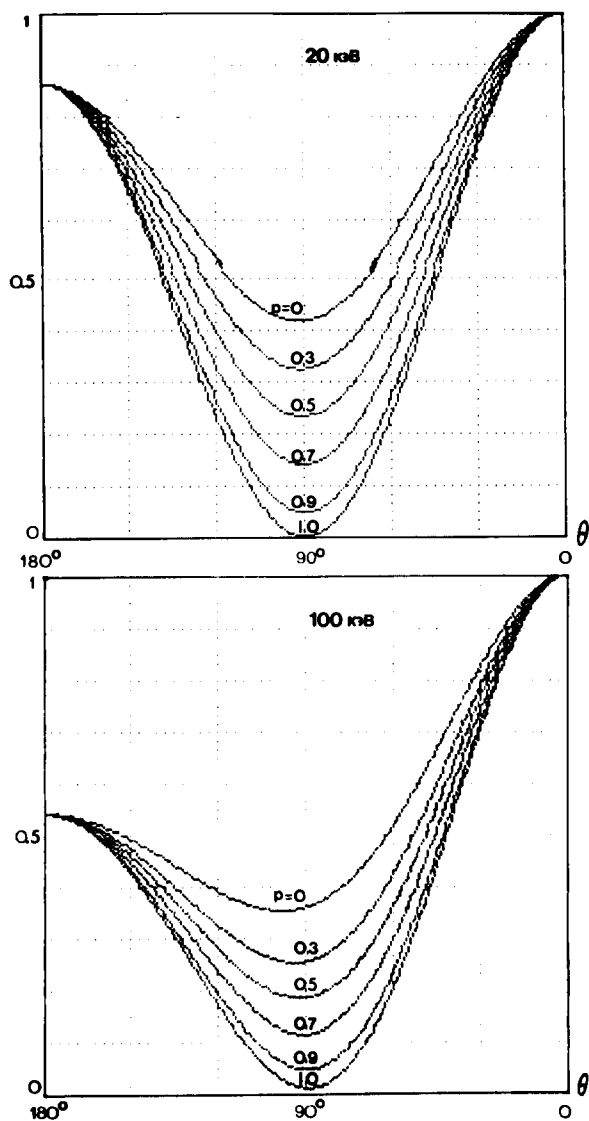


Fig. 6. Compton scattering diagrams for 20 and 80 keV excitation energy;  $p$  – linear polarization coefficient,  $\theta$  – scattering angle.

lection in the detector from the intense lines located in the other parts of the spectrum then disappears.

During observation of element lines in a matrix consisting of lighter elements, selective detection is achieved by installing absorption filters. Installing a tunable dispersion filter (see fig. 1B) between the sample and detector also proves to be effective. In this case, the analysis of 1–3 elements can be performed for one step of retuning. The ultimate case of selective detection is the employment of wavelength-dispersive schemes (fig. 1C) with an energy resolution close to the natural width of the X-ray spectral lines.

*The use of SR polarization:* Plots of the elastic and

Compton scattering (fig. 6) of the exciting radiation have a minima in the the depth which is determined by the polarization coefficient and the selected value of energy. By placing the detector in the plane of the  $E$ -vector of the monochromatized SR beam at an angle of  $90^\circ$  to the beam, one can lower the intensity of the elastically scattered and the Compton peaks and consequently decrease the background plateau height (fig. 7).

With 100% linear polarization the ultimate accessible value of the background suppression  $n$  is limited by two main effects:

a) a finite value of the detector incident angle  $\Delta\Omega = (a/R)^2$  ( $a$  is the detector crystal radius,  $R$  is the distance between the sample and detector); this effect determines the theoretically accessible suppression value in the small energy range  $E_\gamma \rightarrow 0$ ;

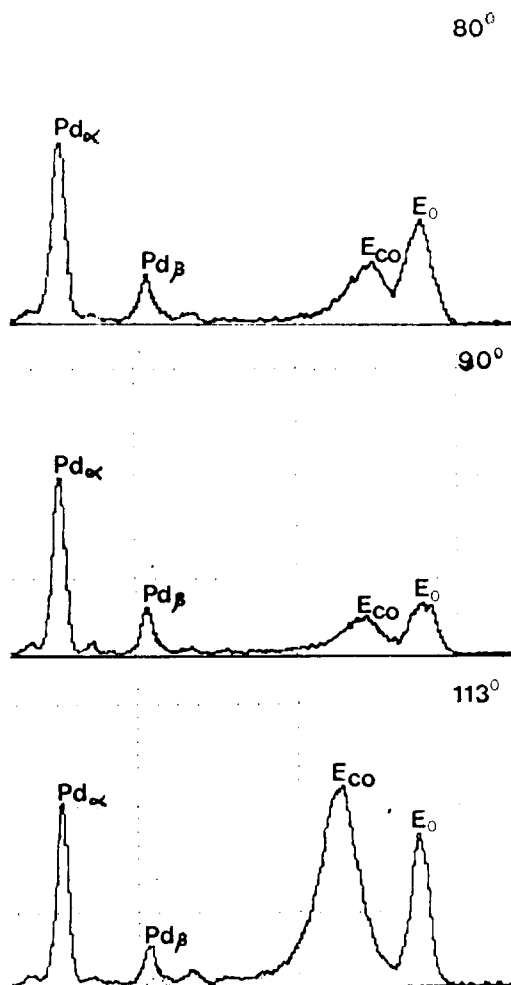


Fig. 7. Relation between intensities of elastic ( $E_0$ ), Compton ( $E_{Co}$ ) peaks and the palladium fluorescent K-lines ( $10^{-3}$  g/g) at registration angles ranging from  $80$  to  $113^\circ$  (silicate matrix). SR from VEPP-3 [7].

b) the small mass of a scattering electron by virtue of which the photon scattering cross section even exactly along the vector  $E$  (exact scattering angle is  $90^\circ$ ) is not equal to zero; this effect determines the theoretically accessible value of the background suppression within the region of high energies

$$n \approx (1 + \epsilon)/\epsilon^2 \quad \text{where } \epsilon = E_\gamma/m_e c^2.$$

Here  $m_e$  is the electron mass and  $c$  is the velocity of light. At a quantum energy  $E_\gamma = 50$  keV  $n < 10^2$ , at  $E_\gamma = 100$  keV  $n < 30$ , and at  $E_\gamma = 150$  keV  $n < 15$ .

In addition, one should take into account the fact that because of either the electron angular spread on the angular instability of the electron beam in the storage ring the linear polarization level averaged over the vertical angle is not equal to 100% even in the median plane.

*Thin samples and scanning:* The large store of excitation power with SR use permits one to decrease substantially the sample thickness. In this case, one can achieve a strong suppression of the secondary processes in the sample such as:

- multiple Compton scattering which considerably expands the Compton peak, especially in light matrices (see fig. 8);
- bremsstrahlung radiation of photoelectrons in the sample;

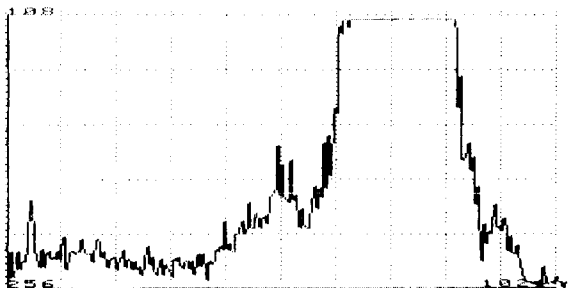
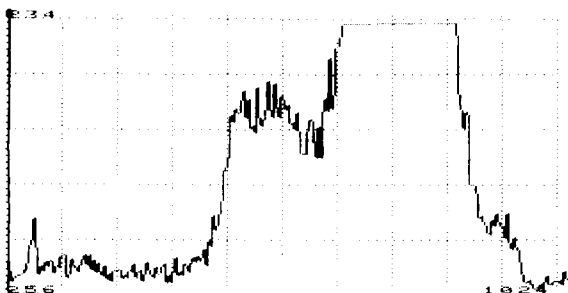


Fig. 8. Spectra of thick ( $100 \text{ mg/cm}^2$ ) and thin ( $10 \text{ mg/cm}^2$ ) samples of paper filters. SR from VEPP-4, excitation energy 75 keV.

- interelement excitation and absorption of fluorescence which requires an interelement correction during the spectrum processing.

However, with a decrease of the volume under analysis, the measurement results can become unreliable, i.e. the elemental composition of the sample of measured size ceases to reflect the mean composition of the object or the etalon.

To increase the “representativeness” of a sample with a high spectrum quality, a scanning procedure is used. In this case, the narrow SR beam excites part of a thin sample, while the sample itself is periodically shifted with a scanner with respect to the exciting beam. The XFA spectra obtained at each step are either added (averaged) or processed by a computer separately [1,7,23,28].

In the last case, one can obtain a picture of one-dimensional [23], two-dimensional or a volume (topogram) distribution of a set of elements in a sample.

## 5. Main requirements for the components of a SRXFA station

In this section we formulate the main requirements and technological solutions which can be used when designing the particular components of a SRXFA station.

*Source of synchrotron radiation:* For XFA purposes it is more convenient to utilize the synchrotron radiation from a wigglermagnet installed on a section of the storage ring with a high value of the  $\beta$ -function. In this case, it is possible

- to obtain more intense and harder SR beams;
- to perform an operational control of the SR hardness regardless of the mode of operation of the storage ring (for example, to suppress the higher orders of the monochromator);
- the small electron angular spread at the point of irradiation (because of the large value of the  $\beta$ -function) permits one to obtain SR with a high polarization coefficient.

In a local analysis for comparatively light elements (with an excitation energy up to 15 keV) the utilization of SR from an undulator without additional monochromatization may prove to be preferable [24].

*Monochromator:* With the use of the selective excitation procedure the transmission band of a monochromator should be several times less than the distance between the absorption edges of two neighbouring elements. For the K-edges this distance is

$$\Delta E/E \approx 2/Z,$$

where  $Z$  is the atomic number of one element. The focusing monochromator with a transmission band  $\delta E/E = (1-5)\%$  can be realized by using mosaic crystals



of pyrolytic graphite (for energies up to 40 keV) and LiF crystals at higher energies [3,7,17].

The best luminosity of a sample is achieved in the single-crystal short-focus scheme. In cases where a high polarization coefficient of the monochromatized SR beam is required, it is preferable to use a one-coordinate (horizontal) focusing, by cutting in advance a certain part of the SR near the median plane with the help of a slit. The optimal width of the slit  $\delta z$  is

$$\delta z = L \delta \theta,$$

where  $L$  is the distance between the slit and the irradiation point, and  $\delta \theta$  is the spread in electron velocities at the irradiation point.

To suppress the higher orders of a monochromator, one can, in principle, employ the cuts of Ge and Si crystals on which the second order of reflection is forbidden; the aperture ratio of such monochromators is not large ( $\delta E/E \approx 0.1\%$ ). The most effective method of suppressing the higher orders is the already mentioned correction for short wavelength SR by varying the magnetic field in a wiggler magnet; this method has been used for XFA on the SR beam from the superconducting "snake" of the VEPP-3 [15]. Another possible solution is the installation of a total-reflection mirror in front of or behind the crystal-monochromator.

If there is no need to select an excitation, it is possible to increase the luminosity of a sample by expanding the transmission band of the monochromator. As shown in ref. [11], in this case a maximum signal/background ratio is achieved at  $\delta E/E = 20\%$ . Such a wide-band monochromator can be composed of a mirror and an absorption filter. Better background conditions in the area of analysis are achieved by a combination of the reflection mirror and transmission mirror [11].

The monochromator design can conveniently include a number of electromechanical movements controlled by stepping motors. When using a focusing crystal, a mechanism for its longitudinal movement is needed, which should provide conservation of the focus point on the sample as the energy varies (see fig. 1A). In XFA the necessity arises to correct the SR intensity at the monochromator exit. In quantitative analysis SR flux correction by a variation of sizes is not desirable since it changes the mean polarization coefficient of the beam or the spectral width  $\delta E$  of the exciting radiation. It is more convenient to employ a filter of the "grey-wedge" type, i.e. a plate of variable thickness from a material which has no absorption edges in the selected region of analysis [7], or to correct the intensity by disaligning the crystal-monochromator angle.

The important problem is the radiation stability of the monochromator components. With the use of LiF crystals and mirrors, to increase their service life, it is advisable to reduce the soft component of the incident

SR beam at most by means of filters. No changes have been observed in pyrolytic graphite crystals used for two years on the SR beam from the storage ring VEPP-4.

*Chamber for the sample, collimators and the scanner:* During the XFA process the chamber offers several functions:

- alignment of the SR beam, the given zone on the sample and the field of vision of the detector collimators;
  - absorption of the radiation scattered on the sample and the transmitted SR beam;
  - possibility of performing an analysis for light elements in vacuum or a helium atmosphere.
- Of importance is the choice of a material for the collimators and the inner covering of the chamber. It must provide:
- a minimal Compton scattering (i.e. it must have a large atomic number  $Z$ );
  - the absence of normal fluorescent lines in the region of analysis (this is possible to ensure if there are two or three chambers with different coverings);
  - low vaporization in the vacuum and under the action of radiation.

Over a wide range of excitation energies ( $E_\gamma > 10$  keV) the filling of the chamber with air has no practical influence on the results of the analysis, except for the appearance of a line of krypton which is rarely the element under analysis. In an analysis for light elements an air-tight chamber, vacuum-pumped out or filled with helium, is required. The use of helium seems to be preferable since evacuation by pumping leads to the evaporation of some samples (for example, biological ones) and to evaporation-product pollution of the chamber and the foil of the detector.

Since semiconducting detectors employed in analyses for light elements have very thin beryllium windows, the diffusion of helium through these can cause the deterioration of vacuum in the detector volume. To avoid this, a small lock which is vacuum-pumped out, can be placed between the detector and the helium-filled chamber.

The motors and the other movable units of the scanner should be shock-proof since the microphone effect lowers the resolution of the SCD. During the time of scanner motion (plus the time of damping the acoustic oscillations in the detector body) it is desirable to lock the XFA spectrum counting.

During scanning and in work with small samples when a scanner is employed as an adjusting unit, it is desirable to observe directly at which point of the sample the SR beam arrives. For this purpose the chamber used for an analysis of Moon samples on the SR beam from the VEPP-3 "snake" was equipped with a microscope with a fibrous light guide. The microscope lens was in the chamber, while the eye-piece connected to it by the light guide was in a place convenient for

work. Fibrous light guides with one end covered with luminophore are convenient to control the SR beam position in places of difficult access. When using light guides and other glass optics in the vicinity of SR beams, protective screens remotely controlled should be used since glass darkens under the action of high doses of X-ray radiation.

*Detector and spectrometric amplifier:* Solid state detectors cover a wide energy range (1 to 100 keV and higher) and provide a large solid angle of detection. The latter is of value in analysis of extremely small amounts of material. For energies higher than 40 keV, wavelength-dispersive systems are not very effective and the SSD is the most convenient unit to detect the K-series of heavy elements.

Besides a relatively low energy resolution, the disadvantages of the SSD are its low counting rate, the presence of the escape peaks of fluorescence and the presence of combinatorial lines. Si detectors provide higher quality of spectra in an energy range up to 30–40 keV; the use of a Ge semiconducting detector is preferable in the harder region. Therefore, for example, the SRXFA station on the VEPP-4 is equipped with two interchangeable SSDs jointly covering the detection region from 3 to 100 keV.

The characteristics of an SSD can be considerably improved in the case of constructing a dedicated detector for SRXFA. A possible scheme of such a detector for energies above 20 keV is demonstrated in fig. 9. It comprises a large number (10–100) of Ge solid state detectors placed on one line with a 2–5 mm step. Each SSD should be equipped with a fast spectrometric amplifier and a “amplitude-code” converter. At present, the highest counting rate for a given energy resolution, is provided by analogue processors with non-Gaussian (rectangular) pulse formation [29]. In front of the main SSDs one can place thin Si detectors which generate an inhibit signal in the case of detection of a quantum with a 9.9 or 11 keV energy (fluorescent lines of the K-series of Ge), thereby decreasing substantially the escape peaks in the XFA spectrum.

Orientation of the thin sample at a small angle to the

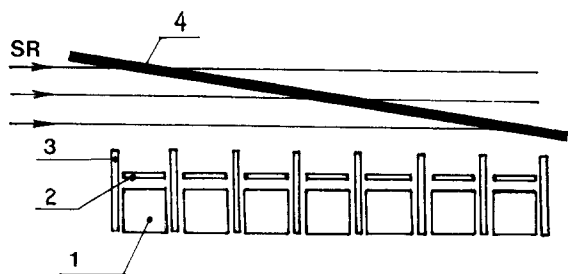


Fig. 9. Multichannel detector for SRXFA. 1 – SSD (Ge), 2 – counter (Si), 3 – collimator, 4 – sample.

beam of the exciting radiation permits one to utilize this radiation for XFA more completely (especially at high energies when the quantum path length in the sample is large).

With the use of a multichannel SSD with  $N$  channels one can improve the characteristic of the SRXFA process: by lowering the intensity of the combinatorial lines proportionally to  $N^2$ , or the time of spectrum collection and the number of scanning steps as  $N$ , or the detection limit by  $\sqrt{N}$  times.

In the soft region ( $E_\gamma < 10$  keV) it is preferable to employ vacuum multichannel wavelength-dispersive systems. At low energies the incident angles of the crystal-analysers become large enough, i.e. the aperture ratio of such a system increases. On the other hand, a close positioning of a great number of emission lines of K- and L-series of different elements makes the use of a SSD with an energy resolution of about 150 eV in effective for an analysis of multicomponent samples.

## 6. Conclusion

As an illustration of the practical application of the technique, we outline below the programme of projects and the main results obtained on the XFA station installed at the VEPP-4 [7]. The X-ray section of the station is shown schematically in fig. 1A.

At present, the following studies are in progress on this station:

### *Geology:*

- an analysis of rock samples, ores and minerals, revision of the standards;
- identification of platinum metals, rare-earths and some other elements poorly identified by the other instrumental methods;
- an analysis of samples with preliminary chemical concentration; with SR use it is sufficient to obtain a small ( $\leq 1$  mg) amount of the concentrate, which is a drastic reduction of the required volume of the sample and the labour content of the process;

### *Microanalysis:*

- an analysis of moon samples (from Luna-16, Luna-24, Apollo-17 missions);
- an analysis of meteorites and monomineral fractions;

### *Biology:*

- a comparative analysis of healthy and nonhealthy tissue;
- a study of the dynamics of the collection and extraction processes of pharmaceutical fractions in a live organism (for example, X-ray contrast substances);

### *Industry:*

- control of material purity in semiconducting production;
- an analysis of admixtures in alloys, purity attestation.

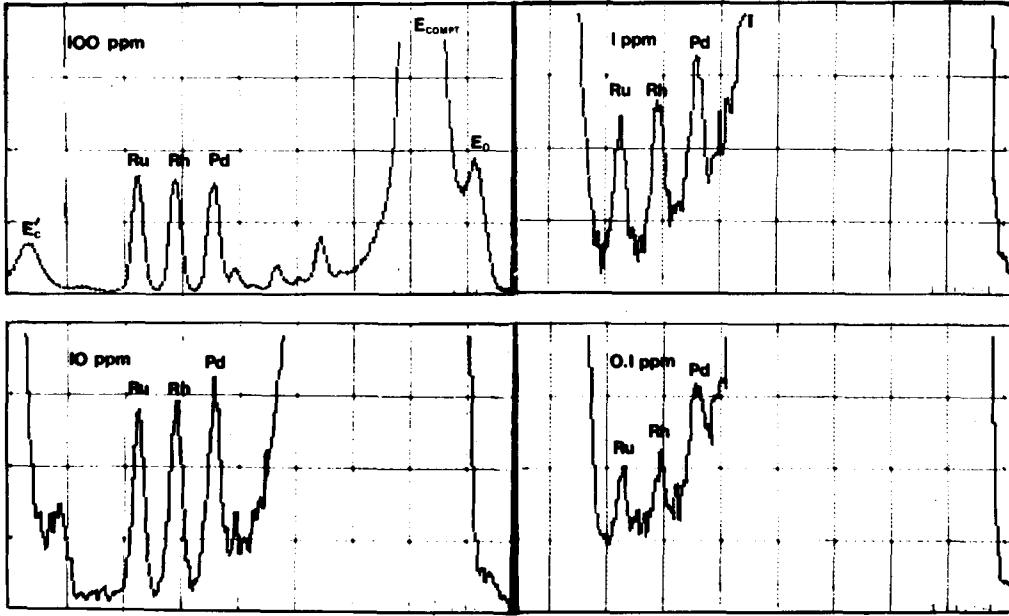


Fig. 10. Light platinumoid spectra in plastic samples with concentrations ranging from 100 to 0.1 ppm (excitation energy is 27 keV, SR from VEPP-4, Ge-detector, counting time up to 1000 s) [21].

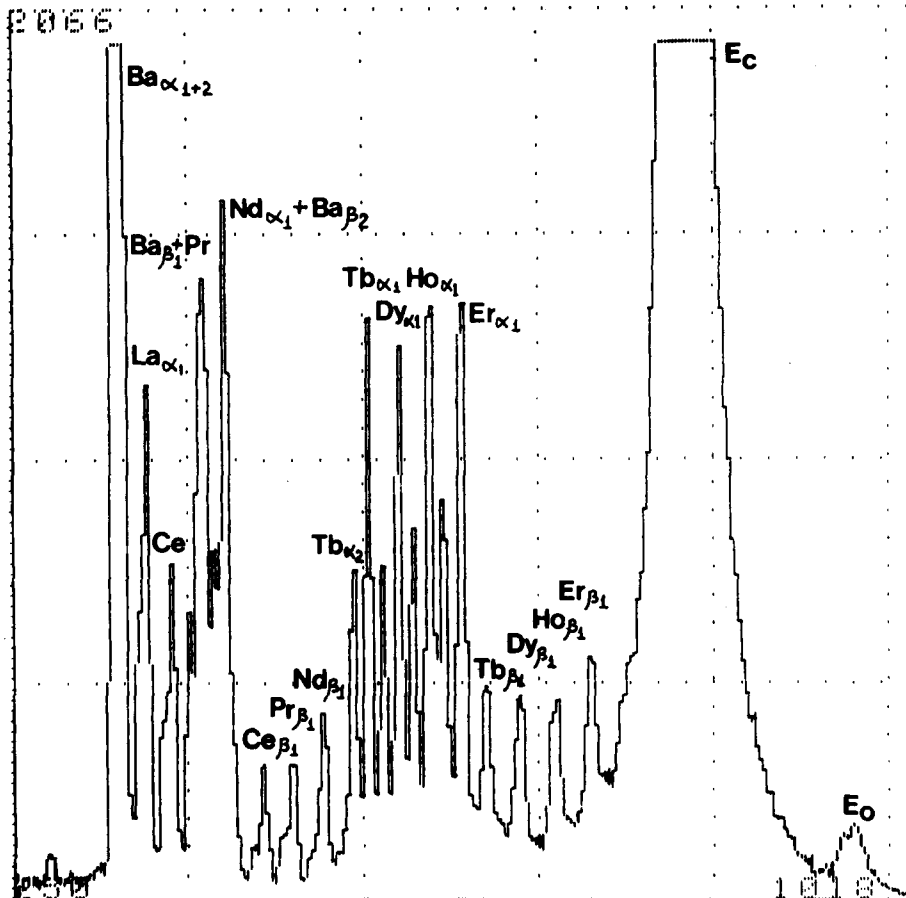


Fig. 11. The spectra of heavy elements with  $\sim 100$  ppm concentrations in a silicate rock (VEPP-4, excitation energy is 75 keV).

The ultimately detectable concentrations of the elements are: 9 ppb in an analysis on Ru, Rh, Pd in pure polystyrol of 50 mg/cm<sup>3</sup> thick (3600 s); 30 ppb in an analysis Rb–Zr and Ru–Ag in rock samples and solutions (10<sup>3</sup> s); 100 ppb in an analysis of light lanthanoids (La–Nd) and 300 ppb in an analysis of heavy ones (Ho, Er) in rock samples (10<sup>3</sup> s). To increase the sensitivity, the analysis of heavy elements ( $E_\gamma > 50$  keV) is performed in thin samples (no more than 50 mg/cm<sup>2</sup>) using the scanning procedure. Characteristic SRXFA spectra, obtained on this station, are shown in figs. 10 and 11.

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