The particularities of using of the hard x-rays (60 – 120 keV) of synchrotron radiation for determination the trace amounts of Rare-Earth elements by the SRXRF method

A. A. Legkodymov, K. V. Zolotarev and G. N. Kulipanov

View Online   Export Citation

ARTICLES YOU MAY BE INTERESTED IN

The Particularities of Using of the Hard X-Rays (60 – 120 keV) of Synchrotron Radiation for Determination the Trace Amounts of Rare-Earth Elements by the SRXRF Method

A. A. Legkodymov [a)], K. V. Zolotarev, G. N. Kulipanov

Budker Institute of Nuclear Physics SB RAS, 11 Acad. Lavrentiev Ave., 630090, Novosibirsk, Russia

[a)]Corresponding author: A.A.Legkodymov@inp.nsk.su

Abstract. The X-ray fluorescence (XRF) analysis with using synchrotron radiation (SR) is a powerful technique for resolving elemental composition of the different samples with high sensitivity. This technique is suitable for nondestructive multi-elemental analyses of heavy elements such as rare-earth elements. In this paper, the choice of optimal excitation energies for the determination of the trace amounts of the different rare-earth elements (REEs) from La to Lu by the SRXRF method was discussed. The SRXRF spectra have received at the synchrotron radiation (SR) station using radiation from the 9-pole wiggler on VEPP-4M at the Siberian Synchrotron and Terahertz Radiation Center (SSTRC). As samples the Russian and international standards of magmatic rocks (AGV-1, BCR-1, DNC-1, BIR-1, SGD-1A, and G-2) were used. This powerful technique should be useful for nondestructive analyses of rare-earth and heavy elements in geological, geochemical and archaeological samples as well as industrial materials.

INTRODUCTION

The determination of rare-earth elements (REEs) a good sensitivity is extremely important, due to the growing need for REEs in today's industry. REEs are an important component in the manufacturing of lasers, catalysts, magnets, fluorescent and superconducting materials. In addition, REEs contain valuable information on rock-forming geological processes that is used in geochemical research.

The Energy dispersive X-ray fluorescence analysis (XRF) is a well-known and widely applied multi-elemental analytical technique, capable of providing reliable quantitative information on the abundance of major, minor and trace amounts of the chemical elements in a variety of materials. The using of the synchrotron radiation (SR) for of the fluorescence excitation dramatically improve the classical XRF analysis capabilities due to possibilities for reduction of the background from scattered primary photons, this become possible, and due to the possibility for choice of the energy of the exited photons [1-3].

The first experiments in analyzing heavy elements according to the *K*-lines of spectra using synchrotron radiation of first-generation sources were performed on the VEPP-4 in Novosibirsk, Russia [4–5]; at HASYLAB in Hamburg, Germany [6]; and with second-generation sources at the NSLS in Brookhaven, United States of America [7].

In the present study we have used high-energy X-rays from SR source. A beamline of the 4.5 GeV storage ring of VEPP-4M (Russia, Novosibirsk) is suitable for producing high-energy X-rays up to 120 keV. We have used of the different excitation energies of X-rays from 60 to 112 keV for SRXRF analysis, which allows us to analyze all REEs from La to Lu utilizing a K series of emission lines. The purpose of the present study is to define of optimal excitation energies for the analysis trace amounts of both the light rare earth elements (from La to Eu, LREEs) and heavy rare earth elements (from Gd to Lu, HREEs) in different samples. Also, we have analyzed of the minimum detection levels (MDLs) of REEs on excitation energies from 60 to 112 keV.

EXPERIMENTAL

This work was carried out at the station of the SRXRF of the VEPP-4M storage ring designed for scientific experiments in the hard X-ray range. Figure 1 shows the layout of the experimental SRXRF station at the VEPP-4M. The synchrotron radiation was generated by the nine-pole wiggler installed in the straight section of the VEPP-4M storage ring. The operating energy of the electron beam in the storage ring was 4.5 GeV at a mean electron current of around 20 mA. The magnetic field in the wiggler was 1.9 T. These parameters ensured a high flux of X-ray photons with an energy up to 120 keV.

The excitation energy of the fluorescence was selected with a double-crystal monochromator working in the parallel (nondispersive) optical scheme. The silicon monocrystals with crystallographic plane (111) are used as energy dispersing elements at the monochromator. The operating Bragg angles of the monochromator for these crystals are 1°–3°, corresponding to adjustable photon energy from 120 to 40 keV, respectively [8].

At the SRXRF station, an energy-dispersing semiconductor detector with a CANBERRA high purity GUL0110 germanium crystal (10.5 mm thick with an area of 100 mm^2) is used to register the X-ray fluorescence spectra; detector resolution ΔE = 125 eV at a photon energy of 5.9 keV, and ΔE = 460 eV at a photon energy of 122 keV. The detector is mounted at 90 to the exciting beam in the plane of SR linear polarization. This is the optimum

direction of detection, at which the background from the elastic and Compton scattering of primary radiation is minimal. Figure 2 shows the experimental setup of SRXRF at beamline №8 of the storage ring of VEPP-4M.

In order to localize the area of analysis on a sample, the monochromatic beam is collimated by tungsten horizontal and vertical slits. The distance from the slits to the sample is 500–700 mm. A conical protective lead or tungsten shield with a 5-mm hole at the center is mounted on the receiving part of the detector. The shield blocks radiation incident on border regions of the detector, which allows us to reduce background noise caused by incomplete charge accumulation in the detector. Also the protective shield absorbs of the background from external scattering. The distance from the receiving part of the detector to the sample is 20–50 mm.

As samples the Russian and international standards of magmatic rocks (AGV-1, BCR-1, DNC-1, BIR-1, SGD-1A, and G-2) were used. The samples were compressed into thin tablets with a surface density of 100 mg/cm^2. The tablets were packed into a specially prepared cuvette consisting of three teflon rings. Mylar film with 5 μm thick was stretched on the rings, providing an almost hermetic seal for the sample.

We didn't use any of the x-ray optics here. The sample irradiated with of the monochromatic x-ray beam with cross-section of 2 mm vertical and 2 mm horizontal.
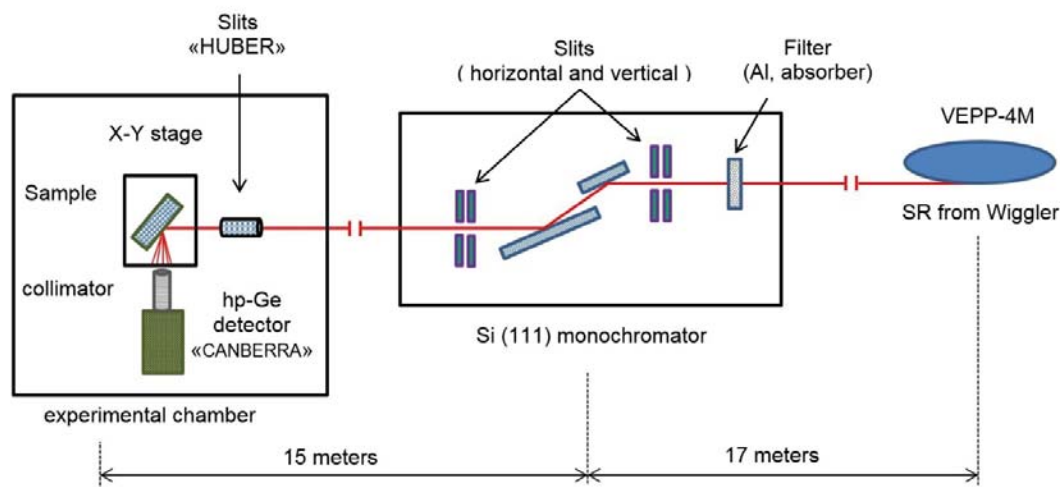

FIGURE 1. The layout of the experimental SRXRF station at the VEPP-4M
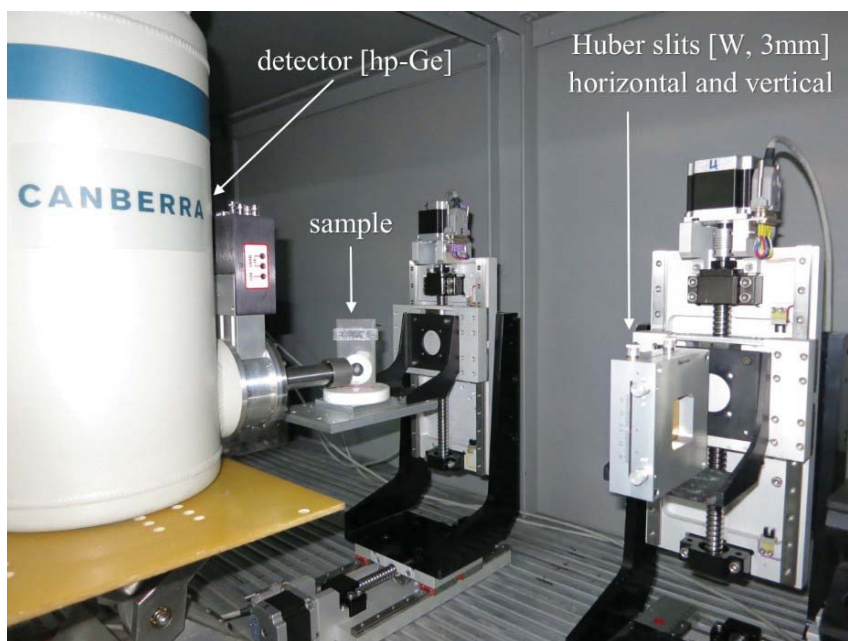

FIGURE 2. The experimental setup of SRXRF at beamline №8 (VEPP-4M)

RESULTS AND DISCUSSION

Figures 3-6 show a typical SRXRF spectra of a geological standard sample (SGD-1A: gabbro, measurement time 600 s). As can be seen in figures 3-6, various rare-earth elements give distinct K-lines. The value of MDL was calculated according to the following equation,

$$MDL = C_0 \cdot \sqrt{I_b}/I_p \qquad (1)$$

where I_b is the background count, I_p is the peak count, C_0 is the concentration of element in the standard sample (the certified value reported in the reference).

Tables 1-4 shows the values of MDL calculated from figures 3-6 for of the different rare-earth elements (REEs) from La to Lu. The data processing of the SRXRF spectra of the figures 3-6 was performed using the AXIL (QAXS) program.

Figure 7 shows the minimum detection limits (MDLs) values calculated from the SRXRF spectra of the figures 3-6. The experimental values for minimum detection limits of rare earth elements from La to Lu are in the range from 100 ppb to 1 ppm.

Figures 3-6 show elastic, Compton, double Compton and multiple scattering for different excitation energies. It is obvious that as the excitation energy increases, the shift between the elastic and Compton peaks increases sharply. So, for the excitation energy of 60 keV this shift is 7 keV, and for the excitation energy 112 keV this shift is 17 keV. In addition, figures 3-6 show that as the excitation energy increases, the shift between the Compton and double Compton peaks increases also. The dip of curve of the background shifts on 6-8 keV to the high-energy region when the excitation energy increases from 60 to 112 keV. So, the further increase of the excitation energy doesn't give a significant expansion of the set of heavy elements for determination with low detection limits.

As can be seen in figure 6, the K-lines W and Pb distinct observe. K-lines W appear from tungsten horizontal and vertical slits "Huber". K-lines Pb appear from of the lead shield block mounted on the receiving part of the detector "Canberra".
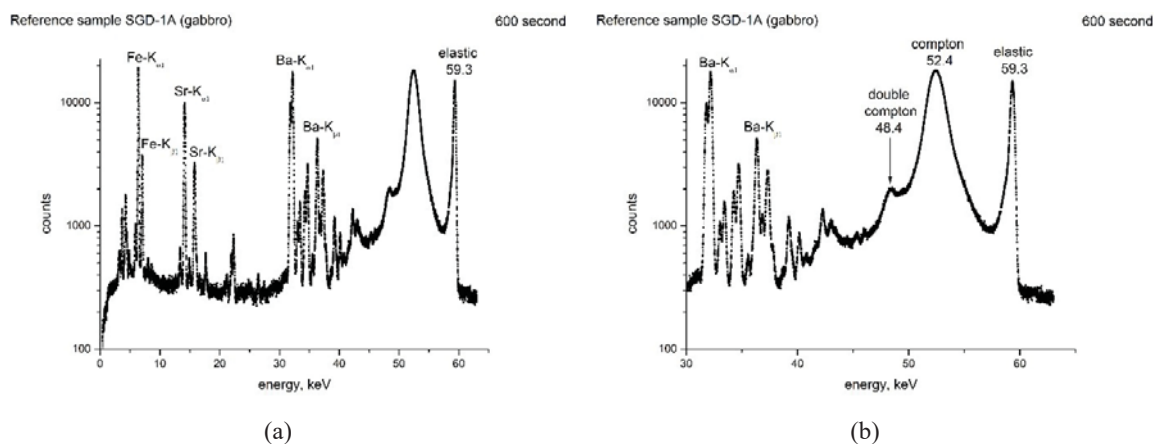

(a)	(b)

FIGURE 3. The SRXRF spectrum of geological sample (SGD-1A gabbro, standard reference sample) excited by 59 keV X-rays and a measurement time of 600 seconds. (a) – full spectrum, (b) short spectrum

(a)	(b)

FIGURE 4. The SRXRF spectrum of geological sample (SGD-1A gabbro, standard reference sample) excited by 72 keV X-rays and a measurement time of 600 seconds. (a) – full spectrum, (b) short spectrum

FIGURE 5. The SRXRF spectrum of geological sample (SGD-1A gabbro, standard reference sample) excited by 86 keV X-rays and a measurement time of 600 seconds. (a) – full spectrum, (b) short spectrum
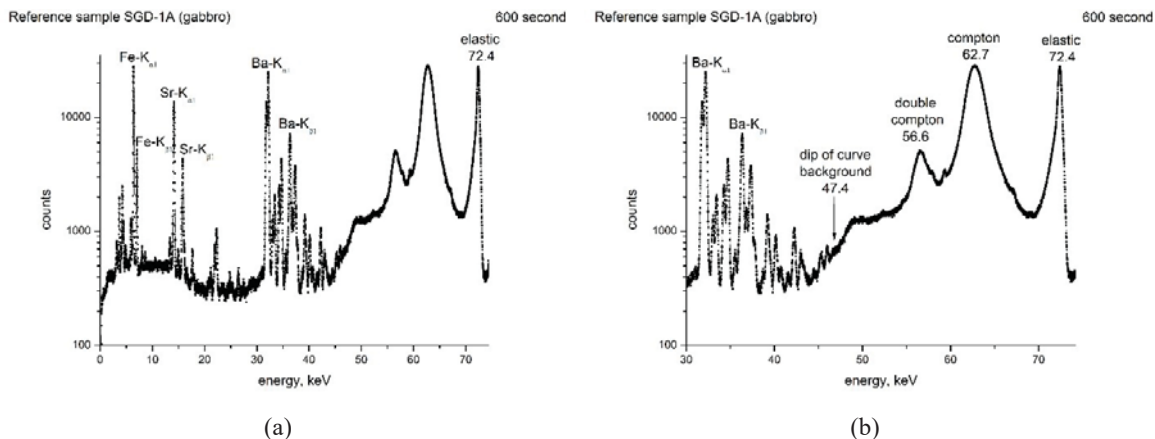

FIGURE 6. The SRXRF spectrum of geological sample (SGD-1A gabbro, standard reference sample) excited by 112 keV X-rays and a measurement time of 600 seconds. (a) – full spectrum, (b) short spectrum
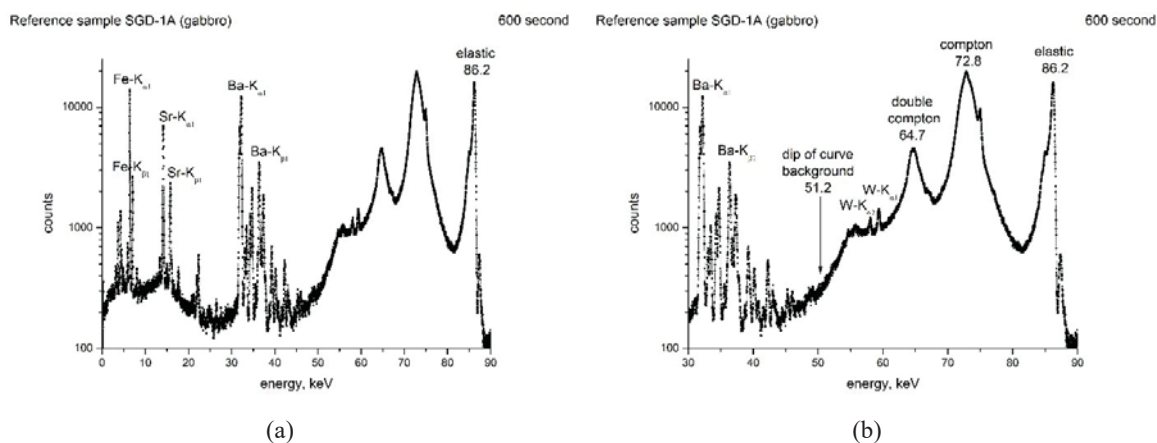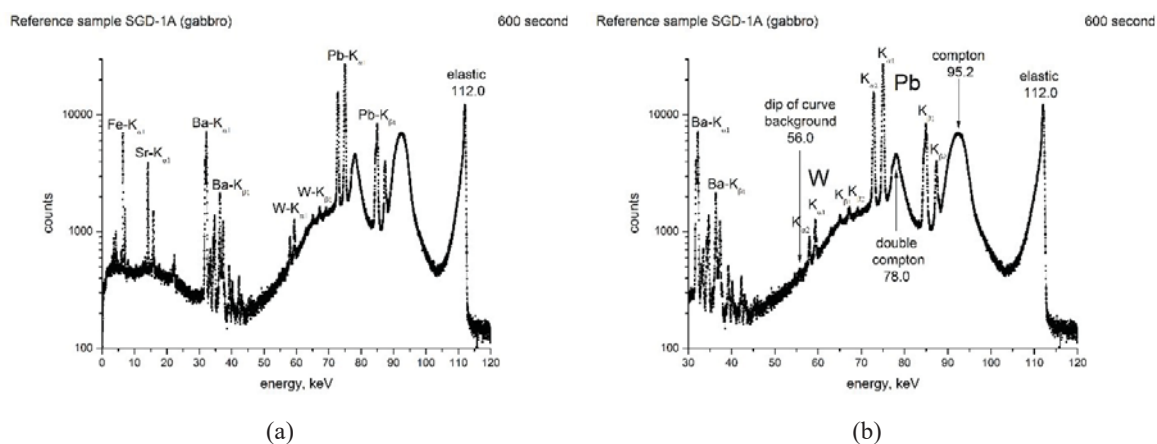
TABLE 1. The minimum detection limits (MDLs) values calculated from the SRXRF spectrum of the figure 3 on the excitation energy 59 keV

Reference sample	Elements	I_p	I_b	C_0, ppm	MDL, ppm
SGD-1A (gabbro)	Ba	1001520	25785	1300	0,62
	La	68849	23526	80	0,53
	Ce	168586	22684	150	0,40
	Pr	15378	29442	15	0,50
	Nd	90770	29876	70	0,40
	Sm	16057	28718	17	0,54

TABLE 2. The minimum detection limits (MDLs) values calculated from the SRXRF spectrum of the figure 4 on the excitation energy 72 keV

| Reference sample	Elements	I_p	I_b	C_0, ppm	MDL, ppm
SGD-1A (gabbro)	Ba	953526	16521	1300	0,52
	La	65921	15742	80	0,46
	Ce	158743	15953	150	0,36
	Pr	19701	16920	15	0,30
	Nd	96911	16696	70	0,28
	Sm	17730	14334	17	0,35
	Eu	3851	15242	5	0,48
	Gd	12441	16524	10	0,31
	Tb	2449	19128	1,4	0,24
	Dy	7474	26686	6	0,39

TABLE 3. The minimum detection limits (MDLs) values calculated from the SRXRF spectrum of the figure 5 on the excitation energy 86 keV

Reference sample	Elements	I_p	I_b	C_0, ppm	MDL, ppm
SGD-1A (gabbro)	Ba	332824	5756	1300	0,89
	La	23738	5702	80	0,76
	Ce	56045	5940	150	0,62
	Pr	7485	5678	15	0,45
	Nd	35095	5246	70	0,43
	Sm	6820	5076	17	0,53
	Eu	1591	5397	5	0,69
	Gd	4317	5688	10	0,52
	Tb	843	6046	1,4	0,39
	Dy	2808	7276	6	0,55
	Ho	547	8204	1,2	0,60
	Er	1695	9540	3,2	0,55
	Tm	228	12754	0,5	0,74
	Yb	793	18243	2,9	1,48

TABLE 4. The minimum detection limits (MDLs) values calculated from the SRXRF spectrum of the figure 6 on the excitation energy 112 keV

Reference sample	Elements	I_p	I_b	C_0, ppm	MDL, ppm
SGD-1A (gabbro)	Ba	191478	7684	1300	1,79
	La	13513	7346	80	1,52
	Ce	32211	7392	150	1,20
	Pr	4218	6951	15	0,89
	Nd	20515	6474	70	0,82
	Sm	3841	6286	17	1,05
	Eu	953	6193	5	1,24
	Gd	2815	6618	10	0,87
	Tb	627	6706	1,4	0,55
	Dy	1863	7134	6	0,82
	Ho	572	7821	1,2	0,56
	Er	1130	9090	3,2	0,81
	Tm	410	10095	0,5	0,37
	Yb	685	11301	2,9	1,35
	Lu	504	13691	0,3	0,21
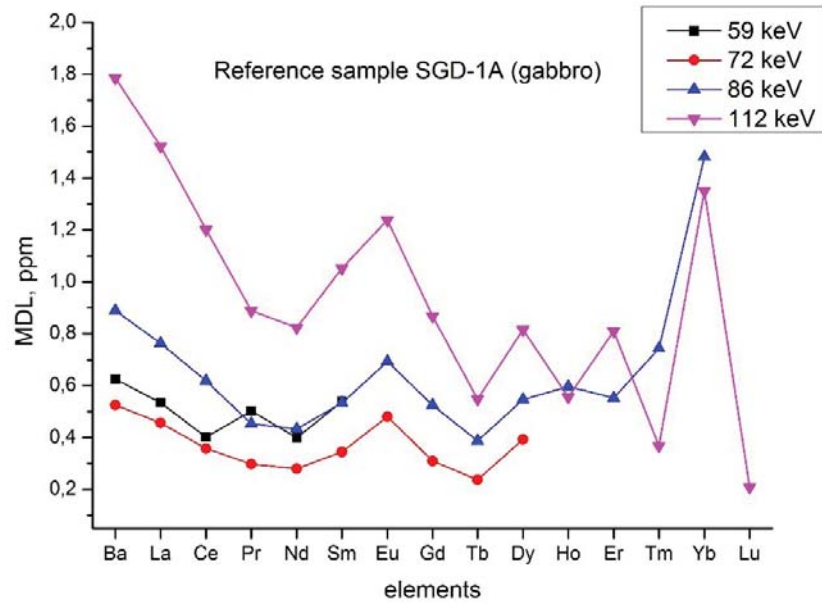
FIGURE 7. The minimum detection limits (MDLs) values calculated from the SRXRF spectra of the figures 3-6.

CONCLUSION

For determination of the trace amounts (less than ppm) of rare-earth and heavy elements by the SRXRF method need that the fluorescent lines of this elements to be locate in range of the low background.

It is obvious that the optimal excitation energies for the analysis of trace amounts of the light rare earth elements (from La to Eu, LREEs) is 65 – 70 keV. For the analysis trace amounts of the heavy rare earth elements (from Gd to Lu, HREEs) it is 86 keV (up to K – edge of Pb). As can be seen from figure 6 (the excitation energy 112 keV), K_β – lines W is situated in range of the high background. K_β – lines W is situated also in the range K_α – lines heavy platinoids (Os, Ir, Pt) and Au. So, even for the excitation energy of 112 keV the heavy platinoids (Os, Ir, Pt) and Au is a very difficult to measure by SRXRF method with trace amounts less than ppm.

The use of hard X-ray optics for a local analysis of samples will significantly reduce the background from elastic and Compton scattering and thereby it increase the sensitivity of the method SRXRF.

ACKNOWLEDGMENTS

REFERENCES

1. I. Nakai, Y. Terada, M. Itou, and Y. Sakurai, Journal of Synchrotron Radiation **8**, 1078-1081 (2001).
2. I. Nakai, "High-energy X-ray fluorescence," *in the book X-Ray Spectrometry: Recent Technological Advances,* edited by Kouichi Tsuji, Jasna Injuk, René Van Grieken (John Wiley and Sons, Chichester, 2004), pp. 355-373.
3. A.A. Legkodymov et al., Bulletin of the Russian Academy of Sciences: Physics **79**, 103-108 (2015).
4. V. B. Baryshev, G. N. Kulipanov and A. N. Skpinsky, Nucl. Instrum. Methods Phys. Res. **A246**, 739-750 (1986).
5. V. Baryshev, G. Kulipanov and A. Skpinsky, "X-ray Fluorescent Elemental Analysis," in *Handbook on Synchrotron Radiation*, edited by G. Brown and D.E. Moncton (Elsevier Science Publishers, Amsterdam, 1991), pp. 639–688.
6. K Janssens, L Vincze, B Vekemans et al., J. Anal. At. Spectrom. **40**, 413-420 (1999).
7. J.R. Chen, E.C.T Chao, J.M. Back et al., Nucl. Instrum. Methods Phys. Res. **B75**, 576-581 (1993).
8. A. A. Legkodymov et al., Bulletin of the Russian Academy of Sciences: Physics **83**, 112-115 (2019).