

ANALYSIS OF MATERIALS

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X-RAY FLUORESCENCE ANALYSIS: STATE-OF-THE-ART AND TRENDS OF DEVELOPMENT (Review)

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The current state of a variant of the method of x-ray spectroscopic analysis — x-ray fluorescence analysis (XFA) — is reviewed. Trends in the development of XFA over the past years are considered. Achievements in the design of instrumentation, developments of theoretical foundations of the method, and new methodologies are discussed.

The history of studies and uses of x-rays spans now more than 104 years. The centenary of the discovery of x-rays has inspired x-ray physicists around the world to hold conferences and publish special collections and monographs dedicated to this remarkable event [1 – 9]. Even now, looking back at that bygone time, one cannot remain unimpressed by the rapidity with which information was exchanged. As is known, W. K. Roentgen, professor, rector of Würzburg University, made the discovery of the new rays on the eighth of November, 1895. Over a period of three weeks, he conducted experiments in his laboratory, and in December, he handed over a description of his results to the secretary of the Würzburg Physicochemical Society. His work has the title “On a new kind of rays: preliminary communication.” On New Year’s Eve, a messenger from the printing house brought a stack of brochures (preprints) to the laboratory. Copies of the work were sent to famous physicists and physicians. Since the equipment Roentgen used in his studies was readily available in many laboratories, it took literally only a few days for his experiments to be repeated around the globe.

The first attempts to apply the new method in surgical research were made within weeks. Thus, in January, 1896, A. S. Popov, the inventor of radio, designed an instrument for generating x-rays. This instrument was made up within two weeks after publication of Roentgen’s paper and was used to identify a small shot in the body of a wounded patient. It is worth noting that during 1896 the number of pub-

lished works concerned with the study of x-rays exceeded 1000. In the “Journal of the Russian Physicochemical Society,” a total of 103 communications dedicated to the “Roentgen” topic were published in that year [2]. On the 25th of September, 1897, in an annex of the city of Irkutsk, Dr. G. I. Multke demonstrated for the first time the principle of operation of the x-ray apparatus. V. S. Kravchenko, a naval medical officer, used, in 1905, x-rays for diagnostic purposes. Staying aboard the cruiser “Aurora” during the Tsushima strait naval battle, he examined forty wounded sailors by a method based on the use of the new rays.

The pioneer of x-ray spectroscopic analysis (XSA) was a British physicist H. Moseley, who noticed, in 1913, that the Cu lines were stronger in intensity than the Zn lines in a spectrum of brass. The practical application of XSA using primary spectra excited by electrons dates back to 1922. In the laboratory of the famous geochemist V. M. Goldschmidt, the first x-ray spectroscopist A. Hudding determined the chemical composition of a number of minerals. Two elements, previously unreported but predicted by D. I. Mendeleev, were discovered using x-rays. In 1923, G. Hevesy and D. Coster discovered the 72nd element — hafnium (Hf), and in 1925, I. Noddack and her husband, W. Noddack, discovered the 75th element — rhenium (Re). The next step in the development of XSA was use of the secondary (fluorescent) characteristic radiation in studies conducted by R. Glocker and H. Schreiber in 1928. This heralded the advent of a new variety of the XSA method — x-ray fluorescent analysis (XFA); technically, XFA was simpler to

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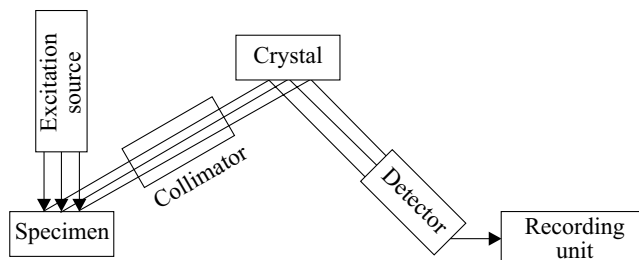


Fig. 1. Schematic diagram of an x-ray spectroscopic unit.

implement, and the detection limit in XFA was one to two orders of magnitude better than in XSA (in the primary spectrum). A detailed description of the foundations of x-ray spectroscopic analysis can be found in numerous works including recent monographs [10 – 21] and review papers [22 – 29]. In what follows, we discuss the guidelines along which XFA has developed with success over recent years. Special emphasis will be placed on the development of advanced instrumentation and theoretical and practical methodologies.

INSTRUMENTATION

The principle of operation of an x-ray spectroscopic unit is illustrated schematically in Fig. 1. From a technical point of view, the important components here are the source of excitation, the crystal analyzer, and the detector. As needed, a filter, a reflector (TXRF version), or a capillary waveguide can be placed between the sources and the specimen. We consider now achievements that have contributed to the potential of the XSA method.

Excitation source. For excitation of x-radiation in analyzed specimens, a variety of techniques are currently employed:

- electrons (electron probe analyzer);
- particles: protons, ions;
- x-ray tube;
- radioisotopes;
- secondary radiators;
- synchrotron radiation;
- laboratory x-ray lasers.

The first two sources are beyond the scope of our review. As regards excitation by heavy particles (Particle-Induced X-Ray Emission Spectrometry (PIXE) method), we restrict ourselves to mentioning data reported in [28]: the number of published XFA papers is more than three times the number of published PIXE papers.

X-ray tube. X-ray tubes are used in XFA as the excitation source. The design and performance characteristics of modern x-ray tubes are well-known. However, for their fabrication at an acceptable level, advanced technologies are needed. For example, a technology has been developed by the Siemens firm that ensures a high level of cleanness at all stages of the technological process of fabrication of x-ray tubes [30]. Modules for fine purification of air, water, re-

agents, and technological equipment were described. In past years, the efforts of researchers were mainly aimed at solving the following problems:

- decreasing thickness of the Be window to 75 μm ;
- developing technologies for obtaining high-purity Be;
- monochromatization of the excitation radiation;
- employment of microfocusing beams;
- generation of polarized radiation;
- development of powerful tubes with rotating anodes (18 kW; Siemens).

A technological achievement was the development of an x-ray tube with an end-face Be window of thickness 75 μm , which provides a way of more efficient excitation of elements with low values of Z . The point is that changeover from the x-ray tube with a side window to the x-ray tube with an end-face window makes it possible to increase the intensity of radiation in the long-wave region of the spectrum by a factor of 2 to 3. An additional advantage is obtained by using Be windows of a thickness of 75 μm rather than 125 μm . Theoretical estimations show that the use of Be windows with $d_0 = 25 \mu\text{m}$ would make it possible to increase the intensity of long-wave radiation in the range of 8 – 20 \AA by a factor of 10 – 100 [31]. These aspects were also considered in [32, 33]; however, the technical feasibility of such a technology remains still problematic. An alternative may be the use of windowless x-ray tubes. This approach was realized in x-ray units operating on the principle of total external reflection.

A topic for active discussion was the potential use of high-purity Be as the material for the tube window, which would increase the intensity of the emitted long-wave radiation. A number of points were elucidated. Beryllium that is available from domestic manufacturers provided a higher intensity of radiation in the wavelength region of 3 – 10 \AA ; however, problems arose with soldering the window to the casing of the tube. Beryllium available from foreign manufacturers with a higher level of impurities provided a solution to this problem and allowed the use of thinner windows. Finally, the emitting efficiency of x-ray tubes in the long-wave region could be improved substantially. At present, when researchers are faced with the necessity of examining samples with substantially smaller concentrations, obtaining a high-purity spectrum of the x-ray tube has become once again an issue of exacerbated concern.

A clear tendency in the design of advanced excitation sources is an increase in power of the emitted radiation. Maximum specific load on the material of the anode mirror (such as Mo, Rh, Ag, or W) is 625 W/mm^2 [34]. A technical breakthrough in the field was creation of an x-ray tube with a water-cooled rotating anode. As reported from Rigaku Denki Co., the maximum specific load for such a tube is 35,000 W/mm^2 , whereas the required power may be as high as 10 (Mo anode; 50 kW; 200 mA) [34] or even 18 kW (an x-ray tube available from Siemens, Göteborg, Sweden) [35]. It should be noted that x-ray tubes with a rotating anode are used in units with total external reflection. A specific fea-

ture to be emphasized is that the positional stability of the focal spot of the rotating anode was excellent. No loss of stability from mechanical vibrations associated with rotation was observed even for focal spots as small as 50 μm and comparable widths of the three slits of the collimation system.

For efficient excitation of *K*-series radiation of elements with high values of *Z*, generators and x-ray tubes were developed that show high operational stability at potentials as high as 100 kV. In this case, the determination of barium and rare-earth elements is simplified substantially.

An alternative concept is that the power required for operation of an x-ray spectrometer should necessarily be reduced. To that end, low-power x-ray tubes have been developed. As examples, one may refer to the "SPARK-1M" short-wave x-ray spectrometer, "Burevestnik" Research and Production Enterprise (required power 250 W); spectrometers available from Philips PW 1660 and VENUS 100 Minilab, with maximum load 200 W (50 kV; 4 mA); also the "Spectroscan" spectrometer, "Spectron" Research and Production (R&P) Association (x-ray tube power 4 W; power required by the instrument 100 W). It should be conceded though that in the latest model from this firm — "Spectroscan-V" spectrometer — the required power is appreciably higher and amounts to 800 W (BK_hV-17 x-ray tube with a Be window 125 μm thick; working voltage up to 50 kV; current strength 0.2 – 6 mA). The spectrometer operates under vacuum, which requires additional power for the vacuum pumping system [36].

Radioisotopes and secondary radiators. Radioisotopes are less powerful excitation sources in comparison to the x-ray tube. A trade-off for the loss in the intensity of excitation when an x-ray tube is replaced by an isotope is that isotope-based sources are energy-dispersive, which makes it possible to dispense with the inefficient component of an x-ray spectrometer — the crystal analyzer. These sources are stable and reliable in operation, suitable for portable use, and can be employed for solving a wide range of analytical problems. At a Denver conference of 1994, a working session was dedicated entirely to the use of the XFA method for studying living organisms under natural conditions [37]. A nonuniform distribution of individual elements in bones within the range of a few centimeters (for example, Pb, with a variation of 20%) was noted. Concentrations were evaluated in relative units considering that the problem of calibration was exonerated. The data obtained are of interest for medicine.

The use of secondary radiators allows the contrast range of tertiary fluorescence to be increased roughly by a factor of 3. Theoretical and experimental estimates show that each event of interaction of the radiation and the target (the scattering material and the incident characteristic radiation) causes roughly a 30-fold decrease in the useful signal intensity, whereas the intensity of scattered radiation with an energy corresponding to this signal decreases by a factor of about 100 [14, 38 – 40]. This variant of monochromatizing the primary radiation is best suited for high-power x-ray

tubes. This technique was used by Canadian researchers for analysis of thin films (0.1 $\mu\text{g}/\text{cm}^2$), where the secondary Mo target was excited by the radiation from ^{241}Am isotope [41].

Synchrotron radiation. This type of excitation radiation provides a very high intensity of the bremsstrahlung spectrum over a wide energy range (5 – 100 keV), which allows a continuous crystal-assisted tuning of the primary monochromatic radiation. The intrinsic polarization of synchrotron radiation (SR) causes a 10 to 100-fold decrease of the background intensity (due to coherent and Compton scattering of the excitation radiation from the specimen) in comparison to the performance of an x-ray tube. Using SR, a high intensity can be achieved in specimens with small dimensions. For example, using a beam with a diameter of 0.5 mm, a sample confined within the beam spot can be analyzed with a detection limit of 0.1 – 0.4 ng at energies of 4 – 35 keV. In practice, bremsstrahlung SR, filtered by an absorber or monochromatized by means of a crystal or an x-ray mirror for excitation of x-ray fluorescence, is used for x-ray fluorescence excitation [15]. Early XFA studies using SR excitation have been reviewed in [15, 22, 42, 43]. We note here that in Russia, a beam of x-ray synchrotron radiation was first produced from a VÉPP-3 storage ring in July, 1973, at the Institute of Nuclear Physics (INP), Siberian Branch of the Russian Academy of Sciences (Novosibirsk). In [42], characteristics of individual SR sources used at the INP were considered and ways of their improvement and fields of application were discussed. In a recent paper of Kulipanov [44], major targets for application of SR in environmental science, geology, geochemistry, and medicine using the VÉPP-3 storage ring were discussed. Among the objects of potential interest for study, the following should be mentioned:

- atmospheric aerosols;
- bottom sediments and water suspensions;
- algae, plankton;
- insects; water suspensions of the Lake of Baikal;
- rocks, lunar soil, Fe-Mn concretions and bottom sediments;
- organs, tissues, blood, plasma.

In 1998, two new SR sources were put in service in Russia, one of which is "Siberia-2," an SR storage ring of the second generation with an energy of 2.5 GeV (I. V. Kurchatov Institute of Nuclear Energy, Moscow). In Novosibirsk, experiments were started using hard x-radiation from an updated VÉPP-4M storage ring with a maximum electron energy of up to 6 GeV.

Since 1995, a new journal on synchrotron radiation has been published [45]. Currently, information on new SR sources of the third generation is available (ALS, ELLETRA, ESRF, Spring-8), they are equipped with advanced general-purpose measuring chambers [46, 47]. Of these SR sources, the most advanced in design is the Spring-8 with an energy of 8 GeV; equipped with a few dozen specialized magnetic systems, it is a universal tool for generating SR with tailor-made properties. Undoubtedly, it

has a clear lead in both the brightness and hardness of radiation as well as in cost (about one billion dollars).

An interesting method for generating an x-ray beam of very small size was proposed by Bilderback and coworkers [48]. It is based on the principle of total external reflection of x-radiation from the inner walls of capillary glass tubes. The inlet and outlet diameter of a tapered capillary fabricated from glass with addition of Pb (with a density of 5.2 g/cm^3) was 22 and $5 \text{ }\mu\text{m}$, respectively; the diameter of the focal spot after 11 – 12 reflections was 360 nm. At present, this diameter is the minimum ever attained for a hard x-ray beam.

X-ray lasers. Development of a highly efficient x-ray laser that would feature high brightness, a high degree of coherence, and a small divergence presents one with a multifaceted problem that can be resolved in a variety of ways. Supported by the latest achievements in technology and theoretical computational potential, the efforts in designing a laser for operation in the x-ray wavelength region expand over a very dynamic field of scientific research [49]. At present, unique large-scale laser units have been developed that allow stable generation in the soft x-ray range using plasma of multiply charged ions. The minimum radiation wavelength achieved lies within a “water window” (2.3 – 4.4 nm), convenient for biological and medical applications of the x-ray laser. The laser effect was also realized in desk-top instruments with rather modest energy and wavelength characteristics and quite available for laboratory research. At present, the efforts of designers are focused on improvement of the beam characteristics and development of new schemes for x-ray lasers that would allow work at shorter wave and pulse lengths. Even now, in brightness and monochromatism the x-ray laser source is superior to the conventional sources of x-radiation — x-ray tubes, synchrotrons, dense laser plasma, etc.

Information about x-ray lasers can be found in papers reported by researchers around the world — from Russia, the U. S. A., Europe, Japan, India, China, etc. [50 – 55]. In a review paper by Andreev and coworkers [55], generation of x-radiation under the action of picosecond laser pulses with an intensity higher than 10^{16} W/cm^2 impinging on solid targets was discussed. The issues discussed were mainly concerned with experimental results obtained in in-house studies (Research Institute of Laser Physics and Institute for Integrated Testing of Optoelectronic Systems). Interesting experimental results were obtained by Gupta [56, 57] in his studies of laboratory-scale x-ray lasers. This author observed optical resonance pumping of the electron K-shell on copper and nickel surfaces by x-ray beams emitted from anodic Cu and Ni materials. Undoubtedly, this is a remarkable achievement of experimental physics; however, its practical use for laboratory analysis remains a remote possibility.

Crystal analyzers. To ensure a higher efficiency of reflection, a surface technology was developed for certain crystals which allowed their reflectivity to be increased nearly by a factor of two without impairing appreciably the

resolving power. Development of multilayer crystals, or pseudocrystals, provides evidence that in certain cases human craftsmanship may be superior to the ingenuity of nature. These crystals are obtained by evaporation of alternating layers of different elements onto a substrate. An advantage of synthetic multilayer structures over crystals is that they can be evaporated onto substrates with tailor-made surface properties and interplanar spacings for a specified range of wavelengths reflected by the given structure. Fabrication technologies of multilayer x-ray mirrors (MXMs) and MXM performance parameters can be found in [58 – 60]. The thickness and material of the layers are determined by the wavelength range for which the given pseudocrystal is intended. For example, for determination of O, F, and Na, sequential layers of W and C are used, for determination of C — layers of V and C, and for B — layers of Mo and a boride. The depth of penetration of soft x-radiation ranges from a few tens of angstroms to 100 \AA . Specifications of x-ray mirrors with grazing and normal incidence were considered in [61], and experimental data on the study of MXMs for soft radiation can be found in [62, 63]. The effect of annealing at $400 \text{ }^\circ\text{C}$ on performance parameters of Mo- and W-based MXMs was discussed in [64]. As was reported in [65], four European companies have combined their efforts to develop mirrors for operation in the hard x-radiation range with a view for their potential application in SR sources of the third generation.

X-ray optics based on the effect of total external reflection. A promising way of improving XFA characteristics is use of the total external reflection of the beam of primary x-ray excitation radiation. To implement total internal reflection, the primary radiation is directed at a very small angle ($2 - 5'$) to the inner walls of hollow capillaries (capillary optics) or to a specimen in the form of a thin film supported on a reflector substrate (the XFA method with total external reflection, TXRF). The reason for this is that in the x-ray region, the refractive index is close to (in fact, slightly less than) unity, since vacuum is the most dense medium for x-radiation [66]. The intensity of reflected radiation at φ close to φ_{cr} is virtually the same as the intensity of incident radiation. The requirements placed on the quality of the surface of the walls of a capillary or a reflector are very stringent: the surface asperity should not exceed $0.1 - 0.05\lambda$, where λ is the wavelength of incident radiation. Quartz glass is used as the material for the reflector. This technique for increasing sensitivity is especially effective when monochromatic excitation radiation, in particular, synchrotron radiation, is used.

Capillary optics. The first practical application of focusing x-ray optics for very soft x-radiation (1 keV) was reported in x-ray astronomy. In 1960, P. Giacconi and B. Rossi (employed at the ASE Research Company, U. S. A.) proposed oblique-incidence mirrors for use in astronomy [67]. They also were part of a research team at the Massachusetts Institute of Technology who designed the first x-ray mirror telescope launched by a carrier rocket for astronomical ob-

servations in space. During the last decade, there has been increased interest in the development of x-ray waveguides. The first experiments carried out in the early 1980s provided very promising results [58, 68]. It was shown in [68] that the output radiation power in a waveguide is determined by optical constants of the material of the capillary wall, and the longer the waveguide, the higher its efficiency. Use of the total external reflection of x-radiation from the inner walls of hollow capillaries allows the generation, comparatively simply and efficiently, of x-ray microbeams. In this technique, the divergent x-radiation from the source becomes collected in a definitely specified region. This raises the possibility of generating beams in diameter from several micrometers to tens of nanometers. Two variants of capillary waveguides for x-radiation are shown schematically in Fig. 2: in one variant, the x-radiation is transmitted through capillaries with a constant diameter (Fig. 2a) [69], and in the other, the x-radiation is focused in a tapered capillary (Fig. 2b) [48]. The inlet inside diameter is 22 μm , and the outlet diameter — 3 μm . Beams 1 and 2 undergo 12 and 11 successive reflections with the resulting theoretical throughputs of 57 and 61%, respectively. The average reflectivity per single reflection event exceeds 95%, and the total angular divergence is 2.3 and 2.2 mrad, respectively.

The main concepts of x-ray multiple-reflection optics based on a special geometry of reflective surfaces have been reviewed in [70, 71]. In particular, Kumakhov [72] proposed elements of x-ray optics based on multiple reflections of x-radiation from bent surfaces. One such variant was coined the Kumakhov lens. Experimental studies of multicapillary optics carried out at the Institute for X-Ray Optics (Moscow) have been reviewed in [73]; the actual state-of-the-art of capillary optics has been discussed in [74, 75].

Results of theoretical and experimental studies of the transmission of x-radiation through capillaries of different type were reported in [76 – 89]. It was shown that the transmission of x-radiation through multicapillary lenses depends substantially on the geometry of the experiment, viz., the effective dimensions of the source, the source – capillary distance, etc. In [90 – 92], evidence on the role of the chemical composition of glass, the quality of reflection surfaces, effects due to the curvature of multicapillaries, etc., can be found. In a review paper by Arkad'ev et al. [93], focusing techniques of x-radiation based on different capillary structures (mono-, multicapillaries, x-ray lenses) were discussed. Effects observed in Kumakhov lenses were interpreted within the framework of geometrical optics. In [85], results of an experimental study of the transmission of x-radiation through quartz capillaries of a focusing capillary scheme in the soft region of the x-ray spectrum were reported. One-piece (monolithic) and compound x-ray lenses for $\text{AlK}\alpha$ and $\text{MoK}\alpha$ -radiation lines were studied and the results obtained were compared with analogous data for multilayer structures. Effects of radiation (in particular, thermal effects) on the performance of the main components of capillary x-ray optics were considered in [94, 95].

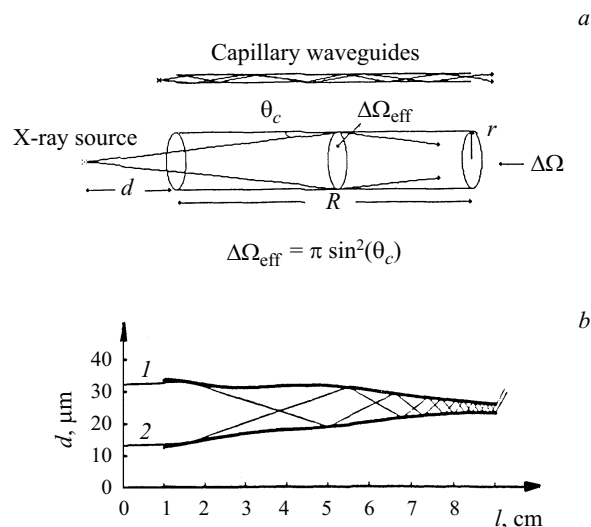


Fig. 2. Schematic diagram illustrating the passage of a beam inside a capillary from a point source (the “effective” spatial angle is determined by a critical angle) (a) and the longitudinal section of a capillary measured under an optical microscope (b).

An explanation of the interference observed in regular capillary x-ray lenses was given in [96] and a formula was derived that relates the radius of curvature of the beam trajectory in each of the concentric rings composed of capillaries to the parameters of the capillaries. It was shown that the spatial resolution of such a system depends but slightly on the radiation wavelength. Using such a system, divergent beams can be converted to parallel beams. The inlet diameter of capillary lenses can be as large as 10 cm. Along with the “concentration” of radiation, the possibility of filtering hard x-radiation arises [91, 96]. The potential use of Kumakhov lenses as analyzers with high spectral resolution or as point sources of excitation for the energy range of 7 – 80 keV was discussed in [90, 92, 97, 98].

Use of capillaries for analytical purposes — (i) determination of trace amounts of elements in the hair and other biological materials with a detection limit of 1 to 100 ppm, which corresponds to about 1 pg [69, 99]; (ii) determination of trace amounts of Ti and Bi in glass and multielement analysis of urban dust and Cu-based pigments dating from the Middle Ages [100]; (iii) mapping of the distribution of trace elements in different materials (with a detection limit of ~ 2 pg for V, Cr, Mn, and Fe) [101, 102]; (iv) distribution of trace amounts of different elements in wood [103]; (v) environmental analysis [106] — was considered in papers [66, 99 – 106].

Spectrometers. At present, a whole range of x-ray spectroscopic units find practical application: scanning crystal diffraction-grating spectrometers; multichannel spectrometers; multichannel spectrometers for analysis of pulp in a flow; combined spectrodiffractometers; small-size scanning crystal diffraction-grating spectrometers; energy-dispersive spectrometers with different detectors; total external-reflection spectrometers; analyzers.

Scanning crystal diffraction-grating spectrometers.

Of the aforementioned types, these spectrometers belong to the general-purpose type. In fact, they represent technically complex, automated analytical units. The number of manufacturers from which these instruments are available is rather limited: the most well-known are Philips (the Netherlands); Siemens and currently Bruker (Germany); ARL (Switzerland); Rigaku (Japan). By way of example, we give performance characteristics of the ARL-9400 spectrometer (required power ~ 7 kW; detection limit for nitrogen $\sim 0.03\%$) and the PW2404 spectrometer (60 kW; 125 mA; maximum of 4 kW for an x-ray tube with a Rh anode; detection limit of 0.2 ppm for Rb, Sr, Nb, Mo). Russia is not found among the commercial manufacturers of instruments of this type.

Multichannel spectrometers. These instruments provide the possibility of simultaneous determination of up to 32 elements within a measuring time of 40 to 100 sec. The parameters of each spectrometric channel are optimized for a specified element. Weak points of this type of instruments are: (i) impossibility of measuring the background intensity on either the right-hand or the left-hand side of an analytical line and (ii) the use of identical excitation conditions for the entire group of elements analyzed. In Russia, an updated version of the SRM-25 spectrometer is commercially available from the "Nauchpribor" Joint-Stock Co. (city of Orel). The instrument has 16 channels and operates under vacuum; the range of analyzed elements extends from F to U. The experimental SRM-27 model has 32 channels. For comparison, the ARL 8660 S spectrometer is equipped with more than 30 channels.

Combined spectrodiffractometers. In metallurgical engineering, there are problems that require knowledge of not only the elemental composition of analyzed samples, but also of the forms of occurrence of individual elements in the sample, that is, the phase composition of the material. For example, in deciding on a rational scheme of processing and extraction of valuable components from iron ore, one must know the mineralogical composition of the raw material and the percentage of hematite (Fe_2O_3) and magnetite (Fe_3O_4). To ensure a steady course of the blast-furnace process, one will want to know the concentration of FeO in the agglomerate, and in the production of aluminum — the concentrations of AlF_3 and Al_2O_3 .

The combined ARL 8600 S instrument houses, in a single casing, an x-ray fluorescence spectrometer and an x-ray diffraction unit for mineralogical and phase analyses [107, 108]. It is supported by the ARL SemiQuant and UniQuant™ programs (analysis of peak and background intensities in specified regions of the total spectrum), which makes it possible to analyze samples of any composition without using standard and calibration specimens.

An alternative solution — the CubiX analytical complex — was proposed by the Philips Co. Its unique feature is that it allows independent determination of the elemental and phase composition of the same sample using two different in-

struments which share a sample delivery system and a software facility for controlling the process of measurement.

Small-size scanning crystal diffraction-grating spectrometers. Instruments of this class — such as the "Spectroscan" desktop scanning spectrometer — are available from the "Spectron" R&P Association (St. Petersburg) [36]. In 1991 – 96, the total sales of these spectrometers amounted to 400. This instrument proved to be the most popular model among crystal diffraction-grating spectrometers of one type offered by an individual vendor.

In 1995, the "Spectroscan-V" vacuum scanning spectrometer ("Spectron" R&P Association) went into commercial production. An innovative feature in the spectrometers of this class was that the specimen could be analyzed outside vacuum confinement, which allowed direct determination of elements from Na to U in materials of any state of aggregation (powders, solutions, gels, etc.) and made sample preparation a less laborious procedure. A trade-off for placement of the radiator in non-vacuum conditions was the short path length of the beam in air (less than 2 mm) and the use of an ultrathin (10 μm) Be entrance window between the vacuum and non-vacuum sections of the instrument. A closed-loop cycle for cooling the x-ray tube and a sealed-off double-chamber proportional detector of x-radiation with a thin Be window (15 μm) were used in this instrument.

The use of a focusing optical x-ray scheme with Johansson crystal geometry provided a high energy resolution: 45 – 60 eV at the $\text{FeK}\alpha$ -line, LiF (200), and 15 eV at the $\text{SiK}\alpha$ -line (PE), which made it possible to reduce effects associated with the overlap of spectral lines. ? Given below are the detection limits for elements from Mg to Ca measured on a "Spectroscan-V" spectrometer with a time of measurement of 100 sec [36]:

Element analyzed	Detection limit, wt. %	Object of analysis
Mg	0.03	Duralumin
Al	0.05	Steel, mortar
Si	0.009	Duralumin
P	0.001	Steel
S	0.005	"
K	0.0007	Mortar
Ca	0.0004	"

The VENUS 100 Minilab x-ray fluorescence spectrometer (Philips), of weight 160 – 200 kg, is intended for determination of Na, Mg, Al, Si, P, S, K, Ca, Fe, Co, Cu, As, Mo, Pb (other sets of elements are available as an option). The productivity of analysis is up to 100 samples per working shift. The instrument has two fixed channels for analysis of Na and Mg; it is also equipped with 12 crystal monochromators for sequential determination of elements (the scattering angle is set by proper positioning of the crystal and the slits). Software is provided with a dedicated program package to control calibration and to make corrections for the mutual interaction of elements; for traditional silicate analysis, a simplified variant for setting the basic parameters is provided.

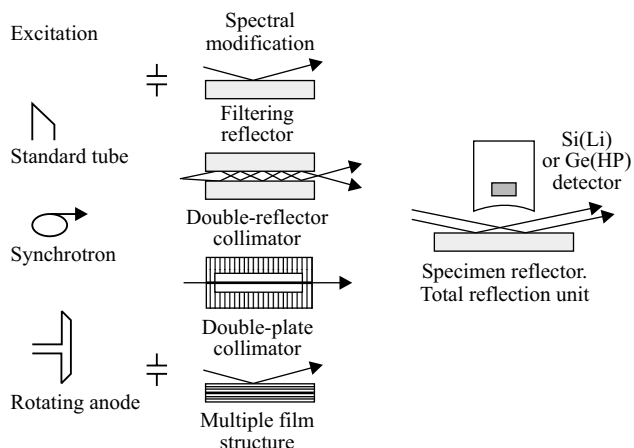


Fig. 3. Variants of spectroscopic units for the TXRF method.

Energy-dispersive spectrometers with different detectors.

Progress achieved in the development of semiconductor detectors [12, 15, 22, 109 – 112] has allowed updating of this type of spectrometers. In place of the traditional cooling with liquid nitrogen, electrically cooled Si(Li)-detectors were proposed for energy-dispersive spectrometers [12]. In the paper of Lechner, et al. [113], a resolution of 225 eV for a silicon detector at room temperature was reported (detector area 3.5 mm²; MnK α -line). Decreasing the temperature to –20 °C improves resolution to 152 eV. A promising model appears to be the portable MiniPal spectrometer (Philips): required power 80 W; nominal x-ray tube power 9 W; an energy-dispersive Peltier-cooled silicon detector (resolution not worse than 250 eV for MnK α -line); elements analyzed — from Na to U.

Detection units based on an electroluminescence gas detector were designed at the “Burevestnik” Research and Production Association for the energy range of 1.5 to 30 keV [114]. The energy resolution of these detection units reaches 8 – 10% for radiation at the MnK α -line and 20% — at the AlK α -line. These detection units are used in the BRA-17 – 01 and BRA-17 – 02 crystal-free x-ray analyzers.

Potential uses of a small-size alpha-proton-x-ray spectrometric (APXS) unit intended for determination of mineral and chemical composition and identification of water in the ground survey aboard the landing modules of spacecrafts were discussed in [115]. The first APXS units were part of the equipment of the Soviet-made “Phobos-1” and “Phobos-2” spacecrafts in 1988.

Spectrometers with total external reflection. Spectral modifications of the units for the TXRF method are shown schematically in Fig. 3 [34]. Efficient monochromatization of the primary spectrum using a special reflector to filter primary x-radiation is illustrated in Fig. 4.

For over a decade, the x-ray fluorescence module has been commercially available, that is, based on the use of the effect of total external reflection [15]. This technique has found wide application in the trace analysis of elements in

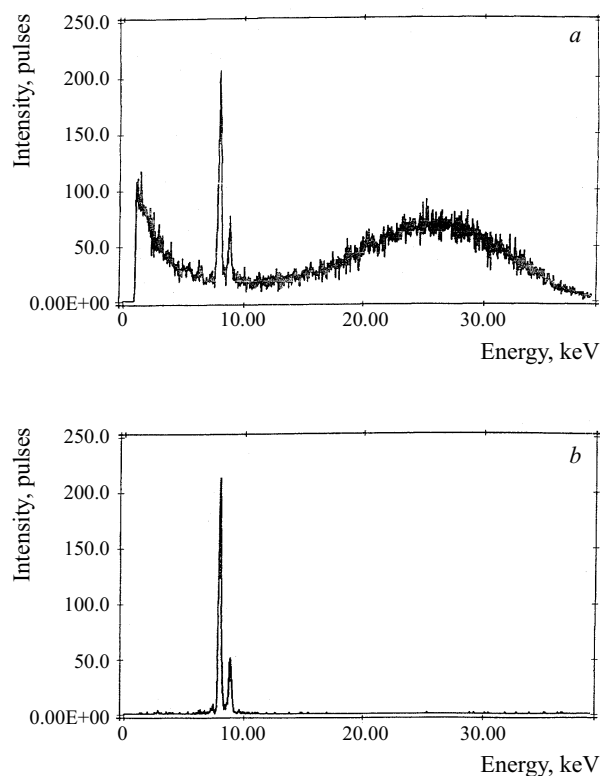


Fig. 4. Spectral distribution of the primary radiation measured without filter (reflector) (a) and with a filter cutting-off the high-energy ($E_c \geq 10$ keV) (b).

geology, biology, medicine, environmental monitoring, etc. (Table 1).

At present, the efforts of researchers in the TXRF field are directed at increasing the efficiency of analysis of light elements (C, O, F, Na) and elements with high values of Z in the K -series, for example, rare-earth elements. We present now a brief review of the results achieved by a team led by P. Wobrauschek (at the Nuclear Institute of Vienna, Austria) that deserves much credit for successfully solving these problems.

A schematic diagram of a spectrometer for recording radiation from elements with small Z using a windowless tube with a Cu anode is shown in Fig. 5 [116]. The angle of incidence of electrons on the anode and the acceptance angle were optimized. Monochromatization of the primary radiation was effected using a LiF crystal with a peak reflectivity of 0.1 – 0.5. A new commercially available Ge(HP) detector with an ultrathin (0.4 μ m) window and a high transparency for low-energy radiation (85% for OK α -radiation) with a resolution of 125 eV at the MnK α -line and onset of a noise peak at 140 eV was used.

The detector area was 30 mm²; the distance between the detector window and the Ge crystal was 2 mm. The back-scattered electrons were captured by means of a magnetic trap. The spectrometer was housed inside a vacuum chamber ($\sim 6 \times 10^{-6}$ mbar), which made it possible to shorten the

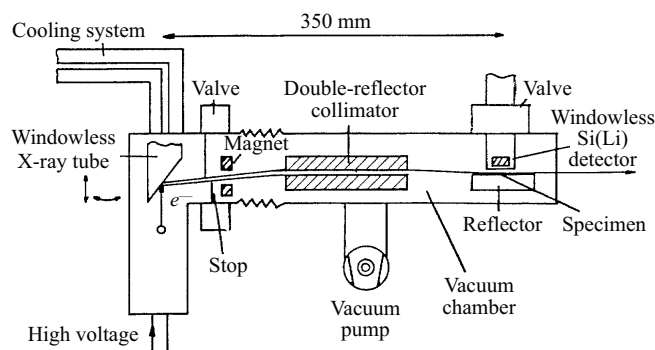


Fig. 5. Schematic diagram of a spectrometer for analysis of elements with small values of Z equipped with a windowless x-ray tube.

distance between the radiation source and the specimen to 130 mm. The intermediate vacuum locking of the specimen protects the x-ray tube and the detector window from damage that might occur because of the abrupt vacuum pressure drop. The detection limit achieved for O was 7 ng or 1 ppm (a concentration in aqueous solution). In [117], the possibility of analyzing light elements from B to Mg was considered. Using an x-ray tube with a Cr anode, the detection limit was found to decrease to 43 ng for C, to 5 ng for F, and to 0.2 ng for Mg. Still lower detection limits (reported by the same authors) were obtained using synchrotron radiation or special x-ray tubes with Mo, Al, or Si anodes.

TABLE 1. Materials Routinely Examined by the TXRF Method

Environment	Water	Potable, effluent, river, snow, sea, rainwater, fog condensate
	Air	Dust particles, aerosols, gaseous dust, exhaust gases, light coal ash
	Soil	Deposits
	Biosphere	Leaves, grass, algae, plants, vegetables, fungi, roots, needles
Geology		Microcrystals, minerals, rocks
Medicine	Fluids	Blood, serum, cellular water, sweat
	Tissues	Lung, liver, hair, bones, nails
Industry	Petrochemistry	Oils, lubricants, crude oil, fuel, coal, coal ash
	Metallurgy	Metallic and nonmetallic alloys, high-quality aluminum
	Other branches	Thin films of different nature and composition, glass-supported coatings, surficial contaminants of Si wafers, semiconducting materials, ultrapure reagents
		Radioactive compounds, dust from electric furnaces
Archeology		Masonry of ancient Rome, ceramics
Forensic examination		Remnants, tissue particles, fingerprints

The spectrum of a sample containing 100 ng of Se and Sr shown in Fig. 6 was obtained using a spectrometer equipped with a rotating-anode tube. As estimated, the detection limit for Sr at the exposure time of 1000 sec was 0.7 pg. The detection limits obtained for Mn, Sr, and Lu using a standard x-ray tube and a rotating-anode tube (measuring time 1000 sec) are compared in Table 2.

To excite the K -series in rare-earth elements and Ba, the x-ray tube potential should be higher than 65 kV. An advantage of working with K -radiation over the L -series is the better resolution of individual lines and the lack of overlap in the K -series radiation of transition elements. When working with such high radiation energies, rather strict constraints are placed on the parallelism of beams considering that the critical angle for total external reflection is less than $3'$. A collimator of special design was therefore needed to ensure the required divergence of the beam for the excitation energy of 90 keV. The focal spot on the anode should be of the same size as the width of the collimator slit (50 μm). The use of x-ray tubes with the required focal characteristics improves substantially the detection limit.

At present, the TXRF method has attained a definite "maturity" level [27, 28, 112, 118 – 121]. More compact and efficient units of the second generation are currently available to the user from manufacturers (Atomica, Oberschleisheim (Germany), and Rigaku and Technos (Japan)).

Operational stability of x-ray instrumentation.

The long-term operational stability of x-ray instrumentation exerts a substantial effect on analytical characteristics such as reproducibility and correctness, rapidity and cost of the analysis. It stands to reason that, in certain cases, a compromise can be reached by increasing the exposure time or by replicating the measurements. It is clear, however, that the changeover from a measuring scheme "standard — four specimens analyzed — standard" to a scheme "standard — eight specimens analyzed — standard" allows the productivity of analysis to be improved by 10% at least. In a similar manner, the changeover from calibration "once a day" to calibration "once a month" improves productivity by 10 – 20% depending on the time required for a single calibration and the length of the working shift.

In recent years, in updating instrumentation much attention has been given to temperature control. As regards advanced multichannel spectrometers, the monochromator in each of them is equipped with a facility for independent temperature control.

As frequently things stand, solving one problems entails others. For example, increase in the intensity of analytical lines and the operational stability of the spectrometer allowed the minimum time of measurement to be reduced to 10 – 20 sec. Further increase in productivity of the instrument was hampered by the relatively large amounts of time required for replacement of the crystal or the detector, for setting a new goniometer angle, etc. In optically positioned goniometers that lack moving parts susceptible to wear (driving mechanisms, gaps, etc.), the accuracy of positioning is

quite high — 0.0003° 2θ /sec, and the time needed for setting the goniometer in the position corresponding to a new analytical line is less than one second (the maximum rotation speed is 30° 2θ /sec). The overall time of analysis advertised by the ARL Co. is the same for all specimens and amounts to 9 min for 52 elements or 12 min for 60 elements (12 seconds per element). As an innovative feature, the double goniometer for the ARL 8420S spectrometer should be mentioned.

An optimum solution would be to minimize the time spent on auxiliary operations, which can be accomplished by automating the entire analytical procedure including the preparation and replacement of samples. This approach was applied to automated analytical units whose functional components, along with the spectrometer proper and the sample preparation facility, are also robotic systems for handling samples. In one such system, an industrial robot is used; it is located on a support which is mounted on the frame of a spectrometer. Beneath it, a container is placed to which samples are delivered by an air conveyer (manual delivery is also possible). Preparation of a specimen for analysis involves machining and grinding operations of the surface and requires a total time of 25 – 90 sec depending on the material of the specimen. Powdered materials are pressed into pellets or melted with a flux — these operations taking several minutes. The robotic functions include removal of the samples from the container, labeling, inspection of the quality of the processed surface, placement of the specimen in the loading device, placement of the loading device in position for measurement, operation of unloading after measurement, sorting of the specimens according to the results of analysis. All operations performed by the analytical unit are controlled by a computer. Productivity of an ARL XRF 8600-SMS-800 analytical unit is 29 analyses per hour (the acquisition time of a single spectrum is 30 sec) allowing for the operations of analytical surface control and specimen labeling; without these operations, the productivity is 40 analyses per hour (the regime for analysis of pelletized samples).

THEORETICAL FOUNDATIONS OF X-RAY FLUORESCENCE ANALYSIS

Theoretical aspects of x-ray fluorescence analysis bear on the following:

- numerical analysis of the intensity of the primary x-ray spectrum;
- numerical analysis of the shape of lines of the x-ray spectrum;
- quantification of the fundamental parameters;
- estimation of the element interactions;
- numerical analysis of the fluorescence intensity for heterogeneous samples;
- assessment of the interaction between x-radiation and the spectrometer's components with a view to optimize design parameters of the spectrometer;
- development of techniques for concentration analysis;
- numerical analysis of the x-ray background intensity.

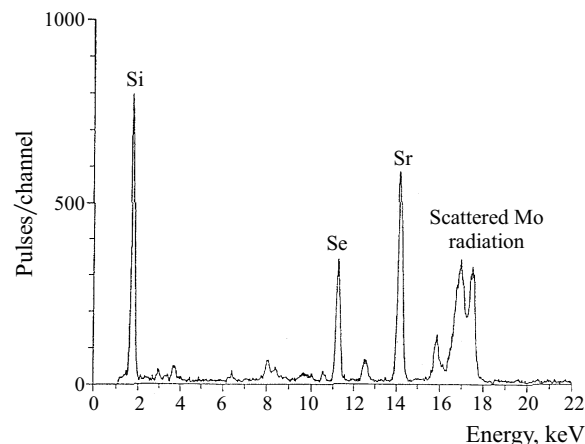


Fig. 6. Spectrum of a specimen containing 100 pg of Se and Sr measured on a spectrometer equipped with a rotating-anode x-ray tube (Mo anode; 50 kV; 200 mA; 500 sec; a multilayer monochromator for separation of $MoK\alpha$ -line radiation).

We discuss some of these aspects.

Intensity of the primary x-ray spectrum. Knowledge of the spectral distribution of primary x-radiation is essential for determination of the exact theoretical intensities of fluorescence. These intensities are used to model the interaction of elements and to analyze errors associated with a change in the chemical composition of samples. Achievements of Pavlinskii and Finkel'shtein and coworkers in the field should be mentioned [122 – 126]. A detailed description of models used for analysis of the spectral distribution of bremsstrahlung and characteristic radiation of x-ray tubes can be found in a study of Borkhodoev [21].

Assessment of the interaction of elements. Currently, staying within a theoretical framework of excitation of fluorescent radiation, one can take account of a variety of matrix effects: contributions due to the selective excitation of atoms of the analyzed element; primary scattering and fluorescence radiation from the sample; subexcitations associated with Auger and photoelectronic phenomena; etc. [11, 13, 15, 21, 127 – 137]. At present, theoretical models for evaluating the interaction of elements are widely used in the development of XFA methods [15, 137 – 140].

Fundamental parameters. Among the parameters of primary interest for XFA, one may mention mass coefficients of absorption and scattering, fluorescence yield, transition

TABLE 2. Detection Limits for Different Excitation Conditions

X-ray tube type	Excitation conditions (anode/kV/mA)	Focal spot, μm	Element	Detection limit, pg
Standard variant	Cu/40/35	40	Mn	0.7
	Mo/50/40	40	Sr	1.5
	Au/100/6	100	Lu	1500
Rotating anode	Cu/40/190	50	Mn	0.17
	Mo/50/200	50	Sr	0.7

probability, relative intensity of individual lines, etc. Unfortunately, the paucity of new experimental data on individual parameters should be pointed out [15, 21, 141 – 164]. Indian physicists deserve much credit for their efforts in this field [143 – 156]. Periodically papers are published whose authors endeavor to revise available data with a view to establish better approximations for a broader range of elements and wavelengths and new implications of absorption coefficients in the numerical analysis of theoretical intensities [15, 21, 166 – 198]. In [21, 169], a database on emission wavelengths and absorption edges was discussed as was its potential use for methodological developments or as a part of software for application in XFA. Regrettably, it should be noted that domestic laboratories cannot claim much achievement in determining fundamental parameters. It is clear that the use of data reported by foreign researchers — such as fluorescence yields, transition probabilities, relative line intensities, mass coefficients of absorption and scattering — cannot raise objections. However, there is little sense in predicting certain performance characteristics of domestic x-ray tubes with their specific designs and geometries — for example, dependence of the reflectivity of a crystal analyzer on the wavelength and intensity of individual lines in different orders of reflection — based on experimental data obtained on x-ray tubes of foreign manufacturers. Theoretically, one may surmise that lone enthusiasts of x-ray tube design as well as specialists concerned with the development of standard composition specimens will have ample area for application of their endeavors for decades to come. Still, users are doomed to “eternal sufferings” by virtue of the familiar law of ever-increasing demands and desires.

METHODS OF ANALYSIS

Over the recent past years, few innovative ideas in XFA methodology have been proposed. The main tendency was refinement of the familiar (classical) analytical methods: external standard; background standard; internal standard; addition method; regression methods; Lachance – Trail method; Raspberry – Heinrich method; semiempirical equations of relationship; theoretical-correction method; basic-parameter method. Various combinations of these methods were tried, ranges of their applicability were outlined, and optimum conditions for conducting analysis were evaluated [170 – 176].

Much attention has been given to the basic-parameter method [11, 15, 21, 177 – 188]. In this method, the concentration of an analyte is calculated using a full expression for x-ray fluorescence intensity with allowance made for the interaction of elements, spectral composition of the excitation radiation, and, if needed, the scattered intensity. It is important to emphasize that the computational accuracy of x-ray fluorescence intensity is sufficient for solving a broad set of analytical problems. The numerical analysis is carried out by a method of successive approximations. In this method, a single standard is sufficient for calibration.

Using this method gives correct results for samples homogeneous for the radiation of all analytical lines. Variants of this method are successfully used for analysis of fused rock samples and various metal alloys. In this technique, a complete analysis of the sample is required, that is, the fluorescence intensities for all elements present in appreciable concentrations in the analyzed samples are to be measured. The neglect of impurity elements, present at relatively low concentration (0.1 – 0.5%), may cause significant errors in the determination of concentrations.

Modern personal computers allow the needed computations to be conducted with sufficient rapidity. The “Uniquant-2” program ensures, in the so-called “standard-free” analysis (nine “pure” elemental specimens are used!), determination of a total of 78 elements in cases where special standards are unavailable or where the specimens are of irregular shape or the material is available in only small amounts.

Error analysis for the basic parameter method has been discussed in detail in [15, 21, 166 – 169]. It is important to note that, owing to the methodological improvements over the last ten years, the sensitivity for elements with small values of Z increased by two orders of magnitude; accuracy of analysis by the basic-parameter method depends to a significant extent on the quality of available parametric data. The basic-parameter method is rather easy to implement in the case of monochromatic excitation of fluorescence. This can be achieved with fluorescence excited by synchrotron radiation, radioactive isotopes (^{55}Fe , ^{109}Cd), by the use of secondary radiators, etc.

PREPARATION OF SAMPLES FOR ANALYSIS

A general scheme for preparation of radiators (powdered or liquid materials) for XFA can be found in [15, 25]. Here we address briefly individual operations in the preparation of samples for analysis.

The choice of a concrete variant of sample preparation is determined by the type of samples analyzed and by the requirements placed on the given analysis. It stands to reason that simple methods, if they offer acceptable accuracy of determination, are always the preferable choice. For example, the methodology for preparation of samples for TXRF analysis spans a set of techniques from the simplest variant (3 to 5 μl of the analyzed solution are applied dropwise to a Si reflector and dried under an infrared lamp) to complex procedures with preliminary concentration.

In [25], physical aspects underlying various methods of sample preparation for energy-dispersive XFA of natural materials (ores, rocks, soil, deposits, vegetable materials) have been reviewed. Requirements placed on thin-film materials used as substrates and on binders used for preparation of pellets are discussed in detail. Theoretical evaluations of the effect of diluting analyzed samples with a flux on the intensity of analytical lines were also presented.

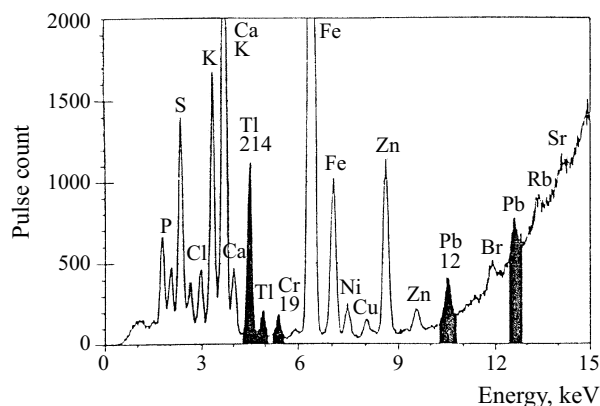


Fig. 7. Spectrum of lung tissue sampled from a patient (a foundry hand) (Mo tube; 50 kV; 38 mA; 100 sec).

In numerous papers, problems arising in different steps of sampling and sample preparation for analysis were discussed: (i) dependence of the intensity of analytical lines on the conditions of pelletizing [189, 190]; (ii) sampling and sample preparation of atmospheric aerosols [24, 191, 192], powdered materials of ferrous metallurgy [193, 194], rolled iron [195], electrode coatings and mixtures for their fabrication [196]; (iii) macrohomogeneity and microheterogeneity of glass radiators fabricated from molten rocks [197]; (iv) effect of organic components on the analysis of molten soil samples [197 – 199]; (v) preparation of thin-layered specimens sampled from marine suspensions on a SYNPOR filter [200]; (vi) stability of glass-like phosphate radiators used for XFA of oxide materials [201]; (vii) automated operations in the preparation of molten radiators [202]; (viii) optimization of sample preparation for micro- and trace TXRF analysis [203 – 206]; (ix) methods for preparation of radiators for XFA of solutions [207 – 213]. Practical recommendations on individual operations in the preparation of various samples can be found in practical guides [214, 215] and review papers [216, 217].

In different schemes, the required time of sample preparation may account for 10 to 95% of the total time of analysis. On the other hand, the error associated with sample preparation may, depending on a number of factors, vary within the same limits. All these considerations reinforce the need for giving special attention to optimization of the sample preparation for analysis.

FIELDS OF APPLICATION

Because of space restrictions, we cannot give the full list of materials analyzed by the XFA method. We confine ourselves to indicating the “target areas of application” specified, for example, for the ARL 9400 spectrometer: petroleum chemistry (petroleum, oil and fuel materials, plastics and polymers); geology and geochemistry (inorganic chemical compounds, refractory materials, noble metals); metallurgy;

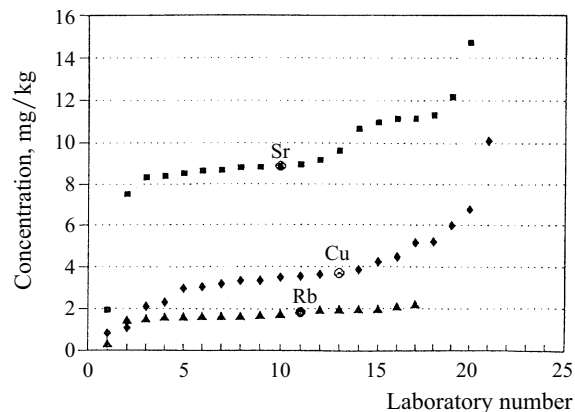


Fig. 8. Results of an interlaboratory experiment (IAEA specimen Lichen-336).

and environmental monitoring. Applications of XFA in academic research and industry were discussed in [218].

Elements that are determined in biological materials by means of XFA are given below:

Material	Elements analyzed
Vegetable materials	N, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ge, As, Br, Rb, Sr, Zr, Nb, Mo, Ag, Cd, Ba, Hg, Pb, Bi, U
Hair	S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Sr, Pb, Hg
Bone	Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Rb, Sr, Zr, Nb, Sn, Pb, U
Liver, kidney, etc.	K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Zr
Blood, plasma, serum	P, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Rb, Sr, Ba, Pb

An important area of application of XFA is direct determination of toxic metals in the organs of living organisms. Whereas the determination of Pb in bones using ^{109}Cd isotope for excitation has a long history, the use of the x-ray tube for fluorescence excitation is a comparatively new technique. In [219], an x-ray tube of specific design with the so-called $\pi/2$ geometry is presented that allows one to obtain a partially polarized radiation. Using this technique, Cd, I, Pt, Au, Hg, and Pb were analyzed in the organs of patients.

The spectrum of the tissue of a lung severely contaminated with dust is presented in Fig. 7 (TXRF, 100 sec) [112]. Peaks shown in black indicate clearly the occurrence of Ti, Cr, and Pb at a level of $\mu\text{g} \cdot \text{g}^{-1}$. In therapy with Pt-containing preparations, platinum was determined directly in patients using ^{57}Co isotope (detection limit 10 ppm). A small sample of the frozen tissue (in volume < 1 ml) was cut off using a microtome. The sample was placed on a nonhydrophobic quartz substrate. Using a micropipette, 5 μl of a solution with an internal standard was added. The sample was dried for 10 min and then measurements were taken at an exposure

time of 100 sec. Tissues sampled from the kidney and the liver were analyzed in a similar manner.

Shown in Fig. 8 are results of an interlaboratory experiment carried out on an IAEA standard specimen (Lichen-336) [112]. Data of the TXRF method are shown by circles. The minimal amounts of material required, moderate expenditure of time, and the possibility of multielement analysis render this approach quite competitive.

Of interest is the method for determination of trace amounts of chemical elements (a total in excess of 20) in healthy and malignant tissues of the human large intestine [220]. The sample (about 400 mg, wet weight) was digested on heating with nitric acid in an autoclave with 100 μg of Te and Y added (as internal standards). The solution (30 μl) thus obtained was evaporated on a quartz slide and the intensity of analytical lines was measured on a spectrometer with total external reflection. In a paper [221] by the same authors, sections of tissues of the human stomach and large intestine were examined. The sample (a 10 μm thin tissue section) was placed on a quartz slide and dried and 10 μl of an internal-standard solution was applied. After drying, measurements were made on a spectrometer.

The XFA method has become a routine technique for pollution monitoring of natural materials [24, 26, 28, 29, 112, 213, 222]. Earlier, we discussed achievements in this area using instruments with total external reflection and synchrotron radiation. This breakthrough has required fundamental changes in the technology of drawing samples and their storage, a revision of the issue of standardization, etc. It should be noted, as a welcome fact, that, manufacturers offer, as an accessory to their instruments, verified or even certified methods of analysis intended for concrete materials. As a rule, software facilities are available at option, which adds somewhat to the cost of purchased instrumentation. However, experience shows that attempts to resolve these issues using home-spun techniques incur still higher costs. A quarter of a century ago when the first attempts were made to couple a computer to an x-ray spectrometer, concerns were voiced that instrument makers may lack sufficient expertise in developing appropriate methods of analysis. However, time has passed, and at present the situation appears to be much less gloomy. For example, over the period of 1995–98, the “Spectron” R&P Association has developed seven methods (certified by the State Committee for Standardization (Gosstandart) of Russia) for quantitative XFA of various compounds and materials including water (natural, potable, effluent), soil, and bottom deposits as well as gases (workspace air, industrial emissions) [223–225]. In [225], certification was reported of a method that was intended for x-ray fluorescence determination of extraneous chemical elements in the affected zone under various traumatic and pathological conditions (M-049-S/98).

As a rule, methods for analysis of industrial materials, raw materials, alloys, soil and geological samples, and objects of forensic examination are based on direct quantification and do not require preconcentration. Still, numerous

methods for analysis of environmental, agricultural, and food products require preliminary certified sample preparation involving the ashing of samples or their conversion to solution, or concentration by means of special sorption filters followed by the measurement of x-ray fluorescence from the material collected on the filter. It takes 20–30 min to increase, by this procedure, the concentration of analyzed elements (Cr, Mn, Fe, Ni, Cu, Zn, Se, As, Cd, Pb, Sn) by a factor of about 1000 and to decrease the detection limit to 0.01–0.001 ppm, which is quite sufficient for analysis (with the exception of Hg). Commercially available from the “Spectron” R&P Association are concentrators, methodologies, and the required accessories (reagents and consumable materials). Similar facilities have been proposed by the “Burevestnik” R&P Enterprise, ARL Co., and other manufacturers.

To conclude, we wish to emphasize that the progress that has been accomplished over the past decades should be attributed not to spectacular achievements of individual researchers, but rather to the persistent endeavors of research teams focused on solving specific problems in x-ray fluorescence analysis.

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