ENERGY DISPERSION X-RAY FLUORESCENCE ANALYSIS FOR ENVIRONMENT PROTECTION
RENTGENA STAROJUMA ENERĢIJAS DISPERSIJAS FLUORISCENCES ANALĪZES PIELIETOJUMI VIDES AIZSARDZĪBĀ

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Abstract. *Environmental monitoring is aimed mostly at pollution levels change tendency estimation and high sensitive analysis methods are applied for this purpose. X-Ray fluorescence analysis (RFA) allows getting information of metal content in ten or hundred seconds. The analyzers with Si(Li) detectors were used for measurements. Our report deals with some examples which are given as new RFA methods (with secondary target) application in the laboratory and field conditions.*

Keywords: X-Ray fluorescence analysis, Si(Li) detectors, analyzing equipment, sensitivity.

Introduction

X-Ray fluorescence analysis is successfully used for determination of composition for various objects (ground, water, air, industrial products). The application of cooled Si(Li) detectors of X-ray emission was appeared particularly promising in RFA, having significant advantages in comparison with other types of detectors.

In 90s years of the last century X-Ray fluorescence analyzers with Si(Li) the detector developed that used measurement method of samples with intermediate thickness by means of a substrate method [1-3]. Do to the high sensitivity of idem equipment and method are used for environmental monitoring.

Environmental monitoring is mainly directed to an estimation of changes in pollution levels. For example, in some cases, methods of high-sensitivity analysis allow to receive the information of the maintenance of metals in 10 or 100 s. Our report considers some examples which are represented as application of RFA methods in a laboratory and field conditions.

Materials and methods

The analyzing equipment, which is used for carrying out energy dispersion fluorescence analysis, involves CRL-7 (the analyzer of x-ray emission) [4]. The CRL-7 includes a sensor and a detector. The sensor contains a source of ionizing radiation manufactured by BSI firm [4]. The detector mentioned has following characteristics: energy of resolution is 160 eV for 5,9 eV quant energy, the area of sensitivity is 30 mm^2 (diameter in mm) and the thickness of the sensitive surface is 4 mm. The rings of radioactive sources, with the data mirrored in Table 1, are used as sources of an ionizing radiation.

Table 1.

The rings of radioactive sources

Isotope	Half-life period	The primary radioactive emission that is used
Fe-55	2,7 years	X-ray emission MnKα 5,9 keV
Cm-244	17,8 years	X-ray emission PuKα 14,3 keV
Cd-109	7,3 years	X-ray emission AgKα 22,6 keV
Am-241	458 years	γ - emission Eγ 59,6 keV

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Standard measured samples are placed in plastic ditches that internal diameter is 30 mm. The plastic ditches have a tightening ring for setting a polypropylene film to the bottom part of a ditch. Primary x-ray radiation passes through a film (the polypropylene thickness is 5 microns). A sample and substrate (that is located above the sample) are excited by primary X-ray radiation. Also, X-ray characteristic radiation of a sample goes through the polypropylene film. The sample represents as a layer of intermediate thickness of the measured object which is placed directly on a film. The metal substrate adjoining the sample is placed above it. This substrate is one of the massive metal disks of pure metal (99,9 %): Ni, Cu, Mo, Sn, Pb, Bi. The disks diameter is 30 mm and thickness is 3 mm.

Besides the sensor the analyzing equipment includes:

- Multispectrum as spectrometric device;
- PC with MCA emulation software and applied software

Approximate position of an ionizing radiation source, the capsule with the measured sample, Si(Li) detector and a substrate are represented on Figure 1.

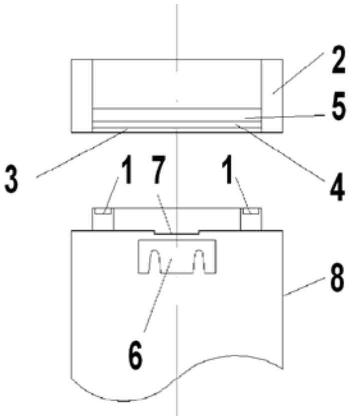

Fig. 1. **Approximate position a of an ionizing radiation source, the capsule with the measured sample, Si(Li) detector and a substrate**

1-The ring of radioactive source (one from Table.1), 2- Plastic capsule, 3- Polypropylene film, 4- The measured sample of intermediate thickness, 5- Metal substrate, 6- Cooled Si(Li) detector (), 7- Window of Be (thickness 12 microns), 8- Cover of the vacuum cryostat

φ - corner between the normal from center of sample surface and the direction of falling primary flow of photons is accepted as equal to 45^o.

ψ - corner of selection for flow of characteristic radiation from the sample. This corner is accepted as equal to 0^o.

Intensity of characteristic X-ray radiation of each i element, which is a part of the homogeneous sample, can be represented as the sum:

$I_x^i = I_1^i + I_2^i + I_p^i$ (1) [5]

I_1^i – intensity of primary fluorescence, quantum/(cm^2*s);

I_2^i – intensity of characteristic radiation (ICR) appeared due to excitation for atoms of each i element. ICP of the elements with are a part of the sample, quantum/(cm^2*s);

I_p^i – ICP for each i element of the sample that appears due to excitation of X-ray radiation of the substrate, quantum/(cm^2*s).

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Value of intensity components for each i element is defined according to the formulae containing in [5, 6].
The full equation (1) is written for each element of multicomponent sample system. That is why, the system of equations is obtained. The obtained system of equations can be sometimes simplifed excepting secondary excitation if its value is so small. The system of equations is usually solved by a method of iterations, i.e. being set by the first set of values C_i (mass concentration of each i element) and calculating its new set (C_1 from I_x^1, C_2 from I_x^2 and etc.). The decision process of the equations commonly converges rather quickly to agreement by a method of iterations. For example, it is usually enough several iterations for solving.

Results

RFA and equipment ensure vanadium detection starting from 15 to 25 g/t in the soil around a power station and from highway ditch. Analysis of soil samples from Riga – Jelgava highway ditch shows ten times higher vanadium concentration level than in the field 100 meters far away from the ditch. Analyzer "CRL – 7" is developed in BSI that allows S, V to be detected and other elements in raw oil, fuel oil and other kinds of liquid fuel. The information of element concentration in fuel allows activities to be conducted for decreasing atmosphere pollution. The same equipment was applied for monitoring of margarine manufacturing process. Margarine manufactured from vegetable oil is in the presence of Ni and Cu catalizators. The catalizator content in intermediate products is a checking index, measurements sensitivity being approximately 3 mg/kg at exposition 800 s. The results received from the measurements have confirmed a possibility to provide required quality of production.
Coal is an important source for reception of energy and will be continued to play a role in satisfaction of energy needs. Coal ash is pollutant of the environment and contains such substances as Al2O3, SiO2, K2O, CaO and Fe2O3. The analysis of the containing of coal ashes with CRL-7 analyzer and using the method mentioned above is shown in Figure 2. The weight concentrations of substances of coal ashes that were accrued from spectrum are represented in Table 2.

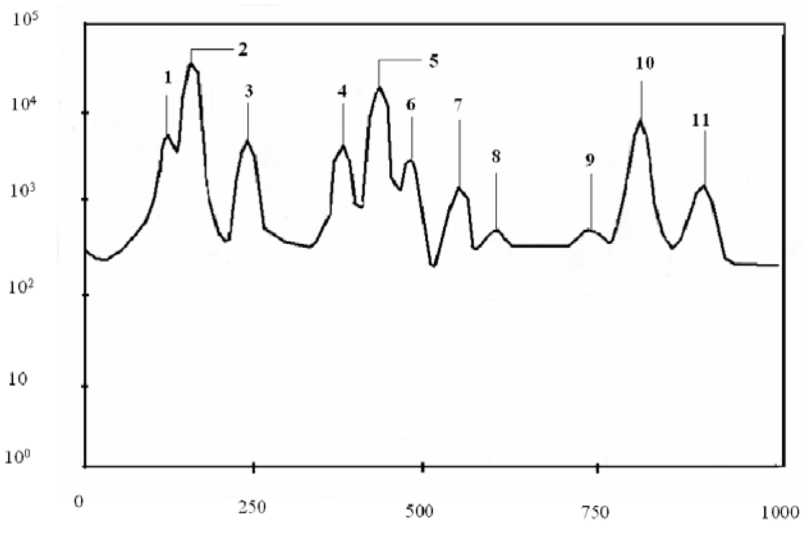

Fig. 2. **A spectrum of coal ashes; Si(Li) detector (Source: Cm-244, Substrate: Cu, LT = 300 s)**

X-ray Emission Energies: 1-AlKα, 2-SiKα, 3-SKα, 4-KKα, 5-CaKα, 6-CaKβ, 7-TiKα, 8-TiKβ, 9-MnKα, 10-FeKα, 11-FeKβ

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Table 2.

Concentration of some substances in coal ashes

Substances	SiO_2	Al_2O_3	Fe_3O_4	TiO_2	CaO	SO_3	K_2O
Concentration, %	47,76	14,72	3,08	1,03	12,08	8,96	1,28

Light particles of substances in the air can be a major case of human diseases and increase the environmental pollution. The elements (such as F, V, Se, Cd, Hg and Pb) polluting the atmosphere can appear from a different number of sources. It is necessary to investigate and supervise levels of their concentration, sources, conditions of spreading and etc.

CRL-7 analyzer has been applied to the analysis of city air. The city air is analyzed deposition in the paper filters with RFA including Mo substrate and the method mentioned above. Approximately 10 m^3/cm^2 of city air was passed through the filter. After that the filters were used as samples for RFA. The spectrum of the covered aerosols is mirrored in Figure 3, but occurred the concentrations are given in Table 3.

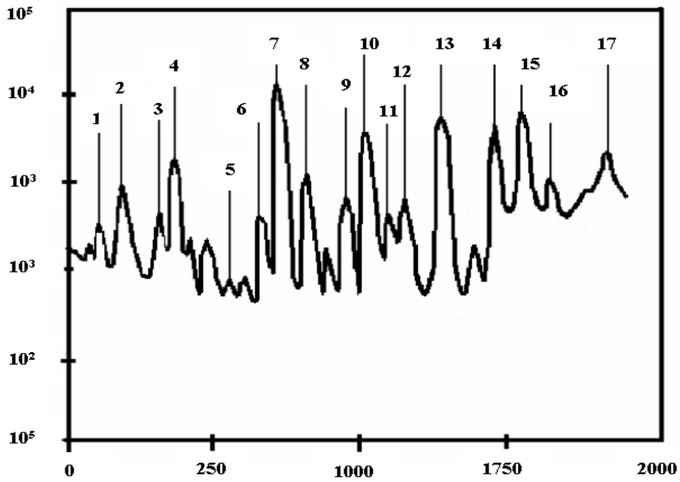

Fig. 3. **The Spectrum of the city aerosols besieged on the paper filter**

X-ray Emission Energies: 1-SiK, 2-SK, 3-KKα, 4-CaKα, 5-VKα, 6-CrKα, 7-FeKα, 8-FeKβ, 9-CuKα, 10-ZnKα, 11-PbL1, 12-ZnKβ, 13-PbLα, 14-BrKα, 15-PbLβ, 16-BrKβ, 17-PbLγ

Table 3.

The concentration value of the elements in city air

Elements	**Si**	**S**	**K**	**Ca**	**V**	**Cr**	**Fe**	**Cu**	**Zn**	**Br**	**Pb**
Concentration, nanograms/m^3	$2*10^4$	$5*10^3$	$8*10^2$	$6*10^3$	$8*10^2$	9*10	$6*10^3$	$2*10^4$	$2*10^3$	$2*10^2$	$2*10^{-1}$

Conclusions

In the course of the new RFA method application in measurement for an environmental (air, ashes) and manufacturing objects (mineral oil and foodstuff) analytical results with high sensitivity, accuracy and low detection range have been received as a result. It gives a technical decision that allows increasing a quality and measurement quickness for control of environmental pollution in future.

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