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Increasing the sensitivity of X-ray fluorescent scheme with secondary radiator using the initial spectrum filtration

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Optimization of the primary filter in the scheme with fluorescent re-radiator was carried out using the minimum detection limit criterion C_{min}. It was established experimentally, that the filtration provides three-fourfold increase for the contrast and 70 % gain for the detection limit. For Au trace impurities in ion-exchange resins, the achieved sensitivity about 1 ppm does not yield to values obtained in the complex Barkla scheme using polarized radiation.

Проведена оптимизация толщины первичного фильтра в схеме флуоресцентного переизлучателя по критерию наименьшего предела обнаружения C_{min}. Экспериментально установлено, что фильтрация обеспечивает трех-четырехкратное повышение контрастности и 70 %-й выигрыш в пределе обнаружения по критерию C_{min}. Для следовых примесей золота в ионообменных смолах достигнутая чувствительность анализа на уровне 1 ppm не уступает реализуемой в сложной схеме Баркла с поляризованным излучением.

1. Introduction

Monochromatization of the primary X-ray spectrum using a fluorescent secondary radiator allows two orders of magnitude increasing the analysis sensitivity for trace impurities in light matrix in comparison to a routine XRF scheme [1–3]. This is actual for investigations in the fields of ecology, medicine, mineral products, extra-pure materials, etc.

As a result of such monochromatization, two main background components remain in the spectrum: the twice scattered (both on the reradiator and the sample) X-ray tube radiation, and the reradiator analytical line Compton scattering on the sample with bremsstrahlung of photoelectrons occurring in the sample under fluorescence excitation [1].

The first background component can be lowered in a given range using a primary filter without substantial attenuation of the working signal, while the second part is inseparably related with the working signal, so this part can not be lowered without the working signal proportional decrease, consequently, without decreasing the concentration sensitivity.

The objectives of the work are the experimental determination of the relations between the mentioned background components, and the filter thickness optimization for spectrum contrast increasing and obtaining the lowest detection limit, C_{min}.

2. Theoretical principles

The primary filter causes attenuation of the fluorescent reradiator analytical lines. An indicator of the attenuation is varying the intensity of the reradiator line scattering on the sample material. The fluorescence excitation of the sample elements are realized by the reradiator lines. So, with filtration of the preliminary spectrum, the concentration sensitivity for the sample *i*-th element, $\partial N_i/\partial C_i$, decreases proportionally to the secondary radiator line intensity or its indicator — the reradiator line scattered from the sample material. Thus, the filtration gives [3]

$$\left(\frac{\partial N_i}{\partial C_i}\right)_F = \left(\frac{\partial N_i}{\partial C_i}\right) \cdot \exp(-\mu_F \cdot \rho\, t), \qquad (1)$$

where N_i — i-th line intensity except for the background; C_i — concentration; ρ and t — filter density and thickness, respectively; μ_F — empirical absorption coefficient obtained from the filter caused attenuation of the reradiator line scattered from the sample,

$$\mu_F = \frac{1}{\rho} \cdot \frac{1}{n} \cdot \sum_{k=1}^{n} \frac{1}{t_k} \cdot \ln\left(\frac{I}{I_{t_k}}\right), \qquad (2)$$

where n — a number of thickness values, t_k, of the primary filter; I and I_{tk} — intensities of the sample scattered reradiator line without filter and with filter of t_k thickness, respectively.

For water solutions, Compton scattering is by an order of magnitude higher than Rayleigh one, that is why the μ_F value can be determined by the Compton line decrease with the filter thickness increasing, and not by the total scattering intensity.

Let us consider the background N_B lowering under filtration. The background consists of two components: a — the X-ray tube spectrum scattered both from the sample and the reradiator; and b — the background related with the reradiator line intensity (the "tail" of Compton scattering at the sample, the scattering at slits and components of the spectrometer, etc.).

The background under the sample i-th line, $N_B = a + b$, with radiation primary filtration can be written as

$$(N_B)_F = \qquad (3)$$
$$= a \cdot \{exp)(-\mu_i \cdot \rho \cdot t) + b \cdot \{exp)(-\mu_F \cdot \rho \cdot t),$$

where μ_i — absorption coefficient of the primary filter material for the sample line wavelength λ_i.

Variation of the detection limit, $C_{min} = 3\sqrt{N_B}/(\partial N/\partial C)$ [4], after filtration, $C_{min\ F}$, with respect to the initial value, $C_{0\ min}$, for the scheme with a secondary radiator, taking (1) and (3) into account is written as

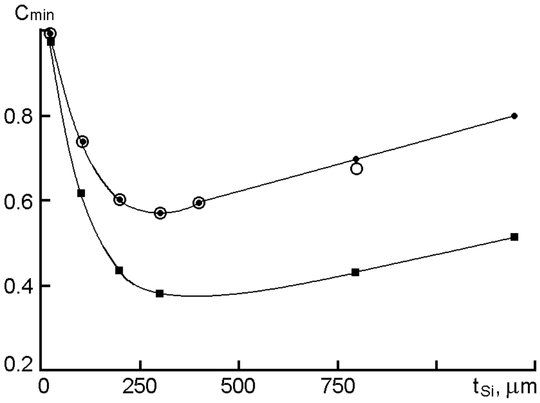

Fig. 1. Cu detection limit dependence on the primary filter thickness. Secondary radiator: • — molybdenum, b/a = 0.25; ○ — yttrium, b/a = 0,25; ■ — molybdenum, b/a = 0.1.

$$\frac{C_{\min F}}{C_{0\min}} = \qquad (4)$$
$$= \sqrt{1 + \alpha \cdot \exp[(\mu_i - \mu_F)x]}\ \exp\left\{\left(\mu_F - \frac{1}{2}\mu_i\right) \cdot x\right\},$$

where $\alpha = b/a$ — the ratio of the background components; $x = \rho \cdot t$ — surface density. Optimization of (4) by x according to $\partial/\partial x = 0$ results in

$$X_{opt} = \frac{1}{(\mu_i - \mu_F)} \cdot \ln\left\{\frac{\left(\frac{1}{2} \cdot \mu_i - \mu_F\right)}{\frac{1}{2} \cdot \alpha \cdot \mu_F}\right\}. \qquad (5)$$

As it is seen from Table 1, the filter optimal thickness for different spectrum parts varies significantly, thus, the selection of the filter thickness is not universal, though is practically independent on the reradiator material.

The filter efficiency for C_{min} lowering in the scheme with a secondary radiator is shown in Fig. 1. C_{min} shows a drastic decrease at the filter small thickness, and it is the more remarkable, the lower is b/a ratio of the background components. Thus, the filtration efficiency increases with decreasing the contribution of the reradiator line

Table 1. Optimal thickness values, $t(\mu)$, of silicon filter to obtain the minimum detection limits for copper and selenium in water solutions. Reradiators: Mo and Y; α = 0.6

Reradiator	Mo	Y
Se–Kα, E =11.2 keV	447	461
Cu–Kα, E = 8.047 keV	268	249

Table 2. Experimental intensities of Compton scattering, analytic lines, and background beneath for a water solution PM 23 standard sample with impurities of 20 ppm content each. C_{min} — detection limit, ppm

Filter + reradiator	Line, +									
	Compton, counts*cdotБ% % %AK* 10^3	Se–Kα			Zn–Kα			Mn–Kα		
		Line, counts	Backgr., counts	C_{min}, ppm	Line, counts	Backgr., counts	C_{min}, ppm	Line, counts	Backgr., counts	C_{min}, ppm
SiO + Mo	68	1250	350	1.25	1050	200	1.00	250	100	4.0
Si 360 + Mo	54	965	150	0.90	850	65	0.6	200	55	3.07
Si 720 + Mo	48	600	95	1.16	600	50	0.77	175	50	3.39
Si 1080 + Mo	38	550	75	1.09	550	40	0.74	150	50	4.24
SiO + Y	83	1600	450	1.11	1520	290	0.83	350	105	2.51
Si 360 + Y	62	1280	160	0.65	1190	82	0.49	250	60	2.45
Si 720 + Y	52	725	100	0.96	725	80	0.83	200	50	2.83
Si 1080 + Y	38	675	75	0.87	650	75	0.90	150	40	3.45

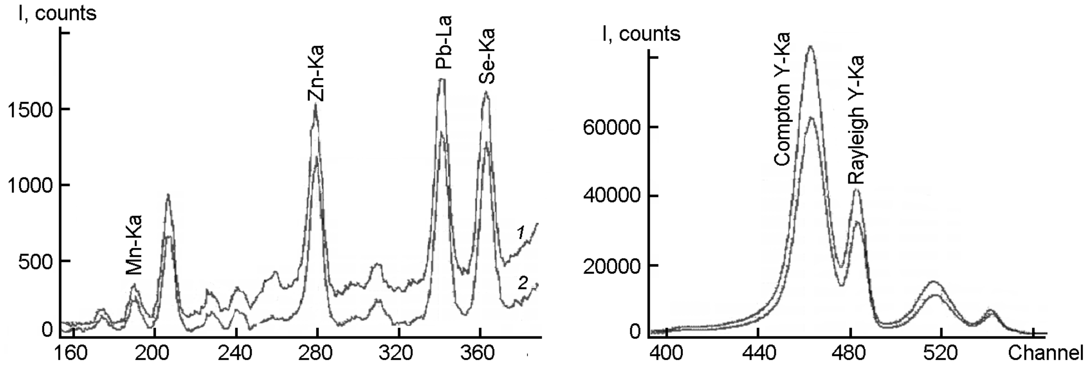

Fig. 2. The spectrum of PM 23 water solution standard sample with Se, Zn, and Mn 20 ppm content. Secondary radiator: yttrium. Exposure 600 s. *1* — without filter; *2* — with silicon filter.

scattered at the sample. If the measurement scheme provides the ratio $b/a = 0.25$, it is easy to reach threefold sensitivity increase according C_{min} criterion, and fivefold contrast increase for a given spectrum line.

3. Results and discussion

In the spectra of water solutions standard samples, there are observed an intense Compton scattering line, a weaker — Rayleigh one (Fig. 2), and analytic lines of trace impurities: selenium, lead, zinc, and manganese. The measurements revealed a line contrast drastic rise with the filter thickness increase and allowed calculating μ_F value by the Compton scattering intensity variation (Table 2). For molybdenum reradiator, $\mu_F = 2.41$ cm^2/g, for yttrium, $\mu_F = 3.16$ cm^2/g. From the results of background measurements under lines at four filter thickness values (0; 360; 720; and 1080 μm) for each analytical line from Table 2, the background components *a* and *b* and their ratio were calculated (Table 3). According to Table 3, the ratio $b/a < 1$ is characteristic only for the lines with energies more 8 keV (Zn–Kα, Se–Kα), thus the filtration may be effective only in a narrow range near the reradiator line.

Let us discuss the increase of the analysis sensitivity through filtration of the pre-

Table 3. The *b/a* ratio of the Compton scattering background, *b*, to the X-ray tube double scattering background, *a*, under different analytical lines

Reradiator	Line		
	Se–Kα	Zn–Kα	Mn–Kα
	11.2 keV	8.63 keV	5.89 keV
	b/a	*b/a*	*b/a*
Molybdenum	0.63	0.58	3.0
Yttrium	0.57	0.87	3.2

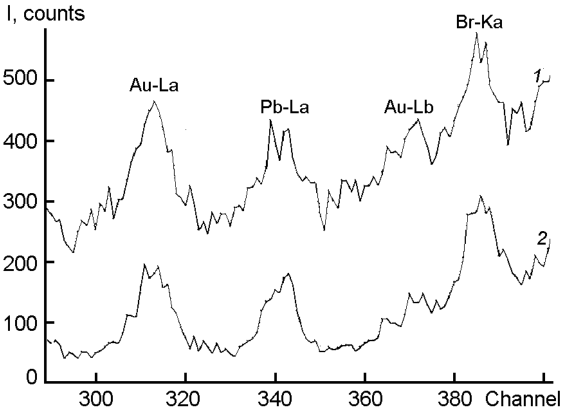

Fig. 3. A spectrum fragment for a standard sample of Au in ion-exchange resin. Au content is 10 ppm. Secondary radiator: yttrium. Filter: silicon. Exposure 600 s. *1* — without filter, C_{min} = 2.1 ppm; *2* — with a filter of optimized thickness, C_{min} = 1.38 ppm.

liminary radiation (Table 2). Though at the $b/a \approx 0.6$ ratio realized in our scheme, we don't succeed to lower C_{min} more than 70 % by "3σ" criterion [4], nevertheless there presents a significant gain (by a factor 3–4) in the contrast of weak signals. For important measurements, it is possible to achieve threefold sensitivity increase due to exposure prolongation. So, the spectrum fragment of gold trace impurities in ion-exchange resins (Fig. 3) shows that the proper filtration (curve *2*) in the scheme with a secondary radiator provides the threefold gain in comparison with the same scheme without filter (curve *1*). The Au detection limit calculated by the curve 2 for Au–Lα line is 1.38 ppm that corresponds to sensitivity values achieved for such objects in Barkla scheme with polarized radiation [5, 6].

4. Conclusions

The optimization of the preliminary filter thickness in the fluorescent secondary radiator scheme was carried out by C_{min} criterion. The filtration was established to provide three- or fourfold increase of the contrast and 70 %-th gain in the detection limit according to C_{min} criterion. For the Au trace impurities in ion-change resins, the achieved 1 ppm sensitivity level does not yield to one realized in the complex Barkla scheme with polarized radiation.

Further sensitivity increase can be reach due to decreasing the b/a ratio of the background components in the experimental spectrum.

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Підвищення чутливості рентгенофлуоресцентної схеми з вторинним випромінювачем шляхом фільтрації первинного спектра

І.Ф.Михайлов, О.А.Батурин, А.І.Михайлов, С.С.Борисова

Проведено оптимізацію товщини первинного фільтра в схемі флуоресцентного перевипромінювача за критерієм найменшої границі виявлення C_{min}. Експериментально встановлено, що фільтрація забезпечує три-чотирикратне підвищення контрастності та 70 % виграш у границі виявлення за критерієм C_{min}. Для слідових домішок золота у іонно-обмінних смолах досягнута чутливість аналізу на рівні 1 ppm не поступається реалізованій у складній схемі Баркла з поляризованим випромінюванням.