

# X-Ray Fluorescence Analysis for Sulfate Ion in Aqueous Solutions by the Dried-Drop Technique Using a Portable Spectrometer

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**Abstract**—The procedure is proposed for X-ray fluorescence determination of sulfate ion in aqueous solutions with preliminary concentrating by the dried-drop technique using a portable energy dispersive spectrometer NITON FXL 959 GOLDD+. The procedure was tested for a wide range of sulfate ion concentrations (10–4200 mg/L) in the course of analyses of groundwater samples from the Over-Jurassic aquifer complex of Moscow region, as well as of the waters draining the sulfide porphyry–copper mineralization of the Nakhodka ore field in Western Chukotka. The procedure was verified by the data of water analyses using ion chromatography and titration techniques.

**Keywords:** natural waters, sulfide ore deposits, sulfate ion, energy-dispersive X-ray fluorescence analysis (EDXRF), portable EDXRF spectrometer, dried drop technique

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## INTRODUCTION

Sulfate ion is among the key components of chemical composition of surface and ground waters. The main sources of the ion are chemical weathering and dissolution of gypsum and anhydrite, as well as the oxidation of sulfur and sulfite minerals. Considerable amounts of sulfate ion are supplied to aquatic formations with industrial and domestic wastewaters. With no technogenic impacts, the concentration of sulfate ion in the waters of watercourses and basins usually varies from several to hundreds mg/L. The concentrations may range up to higher values in groundwaters (as much as thousands mg/L in the areas of sulfide deposits). Increased concentrations of the anion adversely affect organoleptic characteristics and raise the water hardness. The threshold limit value (TLV) is 100 mg/L for fishery basins (The Order..., 2016) and to 500 mg/L for aquatic formations for potable and domestic use (Resolution..., 2021).

Sulfate ion determination in potable, natural, waste, and technological waters along with aqueous extracts of soils and solid wastes is a vital problem of hydrochemistry, environmental geochemistry, and industrial ecology that is resolved in the course of both the analysis of the major component composition of waters and the individual control of the anion content, e.g. when studying the processes of acidic drainage.

A number of techniques are applicable to the analysis for sulfate ion in waters. The gravimetric, turbidi-

metric, and titrimetric methods belong to the specialized procedures based on the precipitation of sulfate ion with barium chloride (less common, with lead nitrate). The measurement ranges of sulfate ion content are within 50–500 mg/L for gravimetry (the arbitrary technique for potable water by GOST 4389–72; RD 52.24.483–2005), 2–50 mg/L for turbidimetry with photometry (GOST 31940–2012; RD 52.24.405–2018), and 10–500 mg/L on average for direct and back titration (GOST 31940–2012; RD 52.24.401–2018; RD 52.24.406–2018). The techniques of ion chromatography and capillary electrophoresis are also widely used. These latter are certified for determining the extended anion composition of water excluding (hydro)carbonate ion and allow one to perform the analyses for sulfate ion including the lowest anion concentrations (FR.1.31.2013.15128; FR.1.31.2018.29956),

X-ray fluorescence analysis (XRF) for sulfate ion in aqueous solutions may be based on the determination of sulfur in the samples and the following conversion into the anion content. The assumption of sulfur occurrence in solutions exclusively as sulfate ion is valid for most of the hydrochemical conditions. The XRF for sulfur in liquid samples is certified only for oil, oil products, and automotive fuel (GOST R 51947–2002; GOST R 52660–2006; GOST ISO 20847–2014). As applied to water, this technique is commonly used in the analyses for major cations and toxic metals (Van

Grieken, 1982; *Sampling...*, 1997; Marguí et al., 2010; Pashkova and Revenko, 2013). However, some of the studies deal with analyses for anions including sulfate ion (Andreeva, 1992; *Sampling...*, 1997). As the equipment used for XRF of waters, not only is stationary equipment used but also portable versions of energy dispersion spectrometers that provide means of in field analyses (Melquiades et al., 2011; Marguí et al., 2012). Portable X-ray fluorescence spectrometers are manufactured by numerous instrument-making companies such as Bruker, Innov-X Systems, Oxford Instruments, Skyray, SciAps etc. and are used intensively for solving a wide variety of problems. The characteristics of spectrometers (X-ray tubes of 3–5 kW,  $U$  within 6–50 kV, and  $I$  up to 200–500  $\mu$ A; the filters of primary radiation; large area silicon drift detectors (SDD) of the resolution up to 150 eV and counting rate up to 200000  $s^{-1}$ ; and the option of blowing with helium) determine the quite low sulfur detection limits for solid samples (0.005–0.01% for a quartz matrix) which provide the ability for successive testing of aqueous solutions after the sample preparation to obtain a solid homogenous concentrate.

This report presents a procedure of X-ray fluorescence determination of sulfate ion in aqueous solutions with preliminary dried-drop concentrating using a portable energy dispersive spectrometer Thermo Scientific NITON FXL 959 GOLDD+ (United States). The procedure was applied to the analyses of groundwater samples collected from the springs over different areas of Moscow region, as well as of the waters draining the sulfide copper–porphyry mineralization of the Nakhodka ore field (the Baimka gold–copper ore zone in Western Chukotka). The procedure was verified by the data of water analyses using ion chromatography and titrimetry.

**The procedure of X-ray fluorescence determination of sulfate ion in aqueous solutions.** The proposed procedure is aimed at sulfur determination using the technique of energy dispersion X-ray fluorescence analysis (EDXRF) in the samples after preliminary concentrating with following conversion of the element into anion content. The most commonly used methods of preliminary concentration for XRF of solutions are the sorption on various substances (activated carbon, cellulose, spheronoxin, ion-exchange resins, and selective membranes), metal precipitation with ammonium pyrrolidine thiocarbamate (APDC), and the dried-drop procedure applied in the course of this study.

The dried-drop procedure is easy and inexpensive: a drop of a tested solution is placed onto a specially prepared filter or a polymer film and dried while adding an inner standard. The inner standard element must be detectable quantitatively under the measurement and absent in the initial solution. The sample preparation procedure enables the samples of small volume (tens to hundreds  $\mu$ L) to be analyzed, while it

is exceeded by other techniques in the degree of concentrating initial solutions.

The determination of sulfur in a solution is based upon the detection of characteristic  $K$  radiation of the element (S  $K\alpha$  2.31 keV) in testing the film of a dried aliquot, the measurement of radiation intensity, the signal correction for the inner standard intensity, and following calculation of a concentration using the calibration diagram plotted by the data of a series of working calibrating solutions.

The analysis of thin films is characterized by the minimum of absorption matrix effects resulting in low background values and hence in improved sensitivity of the measurements. A high content of particulate material, e.g. in riverine and waste waters, complicates that preparation of an emitter in the form of a thin layer, as well as causing matrix effects and decrease of the test sensitivity (Pashkova and Revenko, 2013). To avoid the occurrence of particulate matter, the water should be concentrated after preliminary filtration using membrane filters of 0.45  $\mu$ m pore size.

The main spectral disturbance in the course of analyses for sulfur may be caused by the presence of high concentrations of phosphorus, chlorine (nearby spectral lines, P  $K\alpha$  2.01 keV and S  $K\alpha$  2.31 keV), and lead (the interference of Pb  $M\alpha$  2.35 keV and S  $K\alpha$  2.31 keV). In view of the low solubility of phosphates and lead compounds, the true effect of spectral interference may be seen in the course of testing chloride high-mineralized waters. In this instance, the X-ray fluorescence analysis for sulfur should be carried out after the precipitation of chlorides (e.g., with the equivalent amount of  $AgNO_3$ ). We note that high concentrations of salts in seawaters and brines may complicate the formation of an emitter as a thin layer and cause the increase of the detection limit to 10–30% similarly to the case of particulate matter. The decrease of a sensitivity of the analysis along with matrix effects may be compensated partially by the dilution of a sample.

**Preparation and analysis of samples.** The preparation of an emitter consisted in drying a fixed aliquot of the sample with added inner standard placed onto Mylar film. As the inner standard, scandium was used (the standard sample of scandium solution, Sigma Aldrich 68418,  $974 \pm 6$  mg/kg Sc in 5%  $HNO_3$ ). The mixed solutions for preliminary concentrating were prepared by gravimetry. Using a pipette dozer, 0.4 mL of the sample (the working calibration solution or a water sample) was placed into a polypropylene centrifuge test tube and 0.025 mL of the inner standard solution was added. The liquid in the tube was mixed thoroughly by repeated shaking; using a pipette dozer a solution aliquot ( $V = 0.05$  mL) was then placed as a drop onto the Mylar film ( $s = 4$   $\mu$ m) fixed at the cuvette for the XRF. The drops were then dried in a desiccator at 70°C for 45 min. The placement of a solution aliquot onto the film and the drying were

repeated twice. Thus, the total volume of the concentrated solution was 100  $\mu\text{L}$ .

We note that the analysis of waters containing increased values of calcium ions (hundreds mg/L and over) with no preliminary dilution of the initial sample may complicate the correct determination of the intensity of the inner standard owing to the interference of Sc  $K\alpha$  and Ca  $K\beta$  (4.09 and 4.01 keV, respectively). In view of this, one may either increase the concentration of scandium in the tested solution or use another element as the inner standard (e.g. titanium,  $K\alpha$  4.51 keV).

The prepared emitters were tested using a portable energy dispersive spectrometer NITON FXL 959 GOLDD+. An X-ray tube with an Ag anode (4 W power, 6–50 kV accelerating voltage, and 200  $\mu\text{A}$  maximum current) was used as the X-ray source. The geometrically optimized large area drift detector of large surface area (45  $\text{mm}^2$ ) was used (up to 250000  $\text{s}^{-1}$  counting rate and up to 140 keV resolution for  $K\alpha$  5.9 keV). The device was equipped with systems for sample rotation and blowing with helium (HeliFlush) to improve the detection limits for light elements (from Mg to Cl), as well as with a collimator of X-ray beam selecting a diameter of the measurement spot. The spectra were treated automatically by the algorithms of basic parameters and Compton's normalization using the Thermo Scientific NDT, version 8.4.3 software. The concentrations of the elements were calculated automatically as well by a series of built-in calibrating diagrams that are correctable by standard samples of the composition of a substance with a similar matrix to the tested samples. The data we obtained may be exported to the MS Excel system for following treatment.

In the course of analyses for sulfur, the dried drops were tested under conditions using the Compton's normalization algorithm for the treatment of spectra and with no helium blowing of the measurement chamber. The diameter of a measuring spot was 8 mm, i.e., over the size of a dried drop. Sulfur and scandium (the inner standard) were detected during 60 s under the rated voltage of 20 kV. Each of the samples was tested 3–7 times under the conditions of repeatability and reproducibility. The accuracy of the measurements was selectively controlled using the common standard addition procedure. The measured emission intensities of the elements were converted automatically by the software into their masses using the built-in calibrations acceptable for a saturated layer. The conventional sulfur concentrations in the sample solution ( $C_{[S]}^*$ , mg/kg) were calculated with correction for the inner standard:

$$C_{[S]}^* = \frac{C_{[S, XRF]}^* C_{[Sc]} m_{[Sc]}}{C_{[Sc, XRF]}^* m_{[S]}}$$

where  $C_{[S, XRF]}^*$  and  $C_{[Sc, XRF]}^*$  are the measured concentrations of sulfur and scandium in the film of a dried

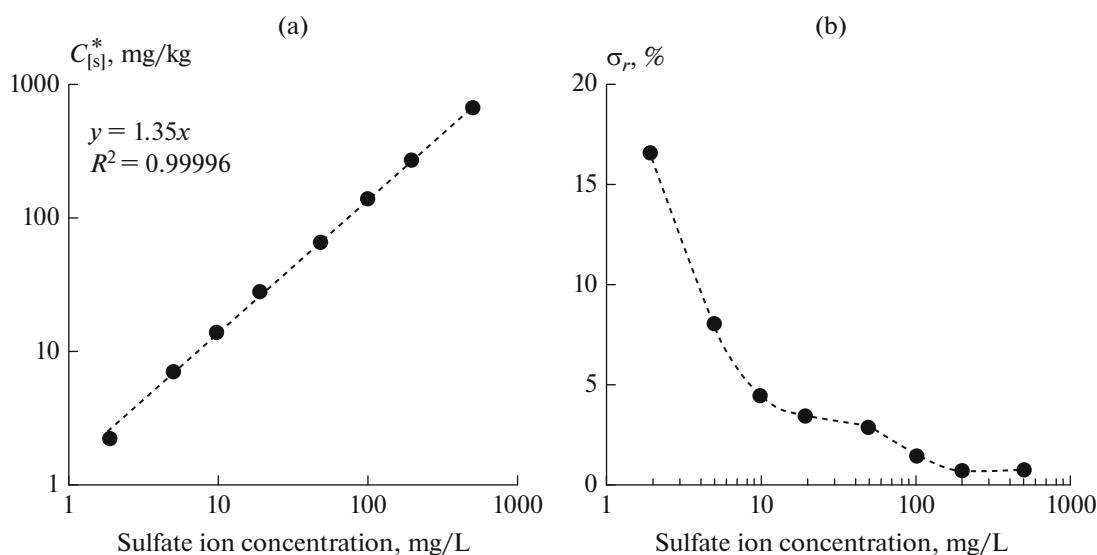
aliquot of the sample solution containing the inner standard, mg/kg;  $C_{[Sc]}$  is a known concentration of scandium in the inner standard solution, mg/kg; and  $m_{[Sc]}$  and  $m_{[S]}$  are the aliquot masses of the solutions of the inner standard and the sample, respectively (g).

The conventional content of sulfur in the sample solution was then converted into that of sulfate ion using the calibration diagram assuming the identity of the densities of working calibration and tested aqueous solutions. The series of working solutions (2, 5, 10, 20, 50, 100, 200, and 500 mg/L of sulfate ion) was prepared by the dilution of the standard sample of 1  $\text{mg}/\text{cm}^3$  mass concentration of sulfate ion (GSO 8746-2006) with double-distilled water, as well as the blank substance. Each of the working samples after the preliminary concentrating was tested at least five times under the conditions of reproducibility. The analysis of the calibrating data set showed its linearity and stability (Fig. 1) thus enabling the use of the proposed procedure for testing waters of various composition.

**Application and verification of the measurement procedure.** The proposed procedure of sulfate determination was applied to the analyses of waters characterized by different compositions: (a) springs located over New Moscow and Moscow region subjected to anthropogenic impact (72 samples) and (b) the watercourses of the Nakhodka ore field (the Baimka gold–copper ore zone in Western Chukotka), 15 samples. The latter waters show the hydrochemical features caused by the occurrence of a sulfide copper–porphyry and epithermal gold–silver mineralization in the drainage basin. The general characteristics of the samples are given in Table 1. The major element composition of the waters at sampling sites is shown in Fig. 2. The composition is represented as Piper's diagram (Piper, 1944) drawn using the program GSS of The Geochemist's Workbench (GWB) software.

The springs were sampled during the summer of 2020. These springs drain the upper aquifer. According to the performed large-scale mapping of hydrogeological conditions in Moscow and Moscow region (Pozdnyakova et al., 2012), the aquifer layers and their separating low-permeable deposits in the upper layer of the extent area of the Moscow and Don moraines are combined into the over-moraine water-bearing complex. All the water-bearing mass that overlies the Jurassic clay constitutes the Over-Jurassic aquifer complex which are regionally widespread. The groundwaters of both the over-moraine and Over-Jurassic complexes over the inhabited areas and industrial zones are polluted and characterized by increased mineralization along with high concentrations of nitrates, toxic metals, and oil products.

The watercourses of the Nakhodka ore field were sampled during the summer season of 2013. Complete analyses of the water composition for major and minor elements were carried out immediately after the sampling (Lubkova et al., 2015). The analysis for sulfate



**Fig. 1.** The results of the analysis of working calibration solutions of sulfate ion using the EDXRF technique: a, the form of calibration set and b, relative standard deviation of measurement results under conditions of reproducibility ( $n$  within 5–9).

ion using the proposed procedure was performed with sample duplicates frozen after preliminary filtration through membrane filters of a  $0.45 \mu\text{m}$  pore diameter and kept at  $-20 \pm 2^\circ\text{C}$ .

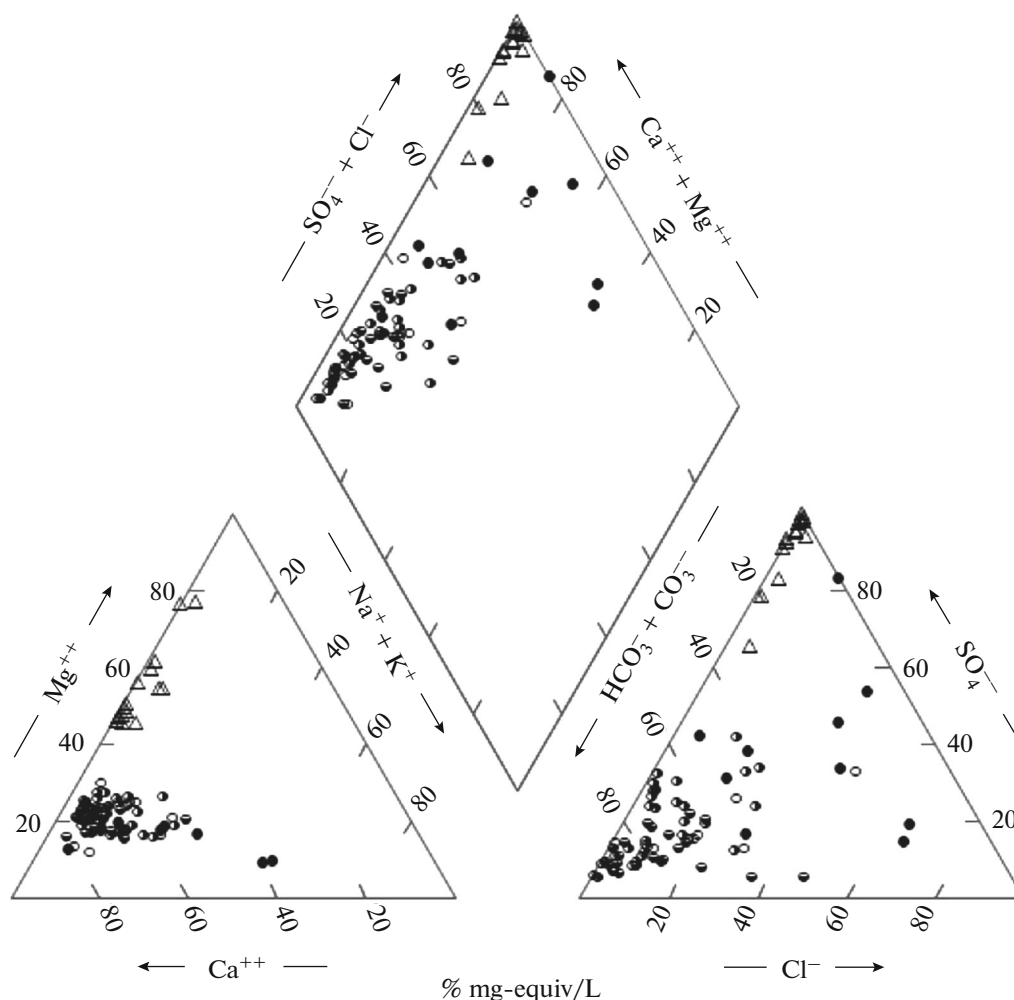
The primary analysis of spring waters for sulfate ion was carried out using ion chromatography using Thermo Scientific Dionex ICS-2000. The surface waters of the ore field were tested by iodometric titration according to the common procedure

(Reznikov, 1954). The concentration of sulfate ion in the tested water samples varied within 11–125 and 77–4216 mg/L, respectively. The data we obtained were used to verify the procedure of sulfate ion determination in the treated water samples by the EDXRF technique, as well as to evaluate the reproducibility of measurements using different techniques by the results of two tests in  $n$  samples according to (*Metodicheskie...*, 1979):

**Table 1.** The general characteristics of the treated samples

Location	Number of samples	Characteristics of water composition
Springs of Moscow region and New Moscow		
Balashikha Urban District	11	0.14–0.85 g/L mineralization; pH 5.4–7.1; the types of waters: chloride–sulfate, sulfate–bicarbonate, chloride and sulfate–chloride, calcium or sodium–calcium; nitrate content up to 54 mg/L
Odintsovsky District	21	0.35–0.77 g/L mineralization; pH 7.2–7.9; bicarbonate calcium type of waters; nitrate content up to 53 mg/L
Pushkinsky District	28	0.12–0.57 g/L mineralization; pH 6.5–7.9; bicarbonate or sulfate–bicarbonate calcium type of waters; nitrate content up to 64 mg/L
New Moscow	12	0.24–0.74 g/L mineralization; pH 6.6–7.7; bicarbonate calcium type of waters; nitrate content up to 60 mg/L
Surface watercourses at the Nakhodka ore field in Western Chukotka		
Watercourses draining copper stockworks and near-ore haloes	10	0.2–5.6 g/L mineralization; pH 3.2–7.5; calcium–magnesium and magnesium sulfate type of waters; highly- and extra highly metallic* by the content of trace elements (total 1–250 mg/L)
Watercourses draining epithermal Au–Ag-mineralization	5	2.2–3.0 g/L mineralization; pH 6.3–7.6; calcium–magnesium and magnesium sulfate type of waters; highly-metallic by the content of trace elements (total 1–50 mg/L)

\* By (Plumlee et al., 1999).



Major components of analyzed water samples

- Springs in New Moscow
- Springs in Balashikha, Moscow region
- Springs in Pushkinsky District, Moscow region
- Springs in Odintsovsky District, Moscow region
- △ Surface waters of the Nakhodka ore field in Western Chukotka

Fig. 2. Piper's diagram representing the major component composition of analyzed water samples.

$$\sigma^{\text{rep}} = \sqrt{\frac{\sum_{i=1}^n (C_{i1} - C_{i2})^2}{2n}}, \quad \sigma_r^{\text{rep}} = \frac{\sigma^{\text{rep}}}{C_{\text{av}}} \times 100\%,$$

where  $C_{\text{av}} = \frac{\sum_{i=1}^n (C_{i1} + C_{i2})}{2n}$  and  $C_{i1}$  and  $C_{i2}$  are the results of sulfate ion determination in the sample  $i$  using the EDXRF and certified procedure (ion chromatography or iodometric titration), respectively.

The concentrations of sulfate ion in water samples determined using the proposed procedure are given in Tables 2 and 3. The relative standard deviations for

sulfate ion determination by EDXRF procedure is 5% on average (at most 10%) for concentrations within 10–50 mg/L and 2% (at most 6%) for the values over 50 mg/L.

Tables 2 and 3 also include the results of primary water analyses for sulfate ion obtained using the procedures of ion chromatography and iodometric titration. The graphical comparison of the data points to the good reproducibility of the results of sulfate ion determination obtained using the EDXRF and other procedures (Fig. 3): the ratios of anion concentrations in the samples are within 0.9–1.1. Discrepancies beyond this range are registered for less than 5% of the spring water

**Table 2.** The results of sulfate ion determination in spring waters using the techniques of ion chromatography (IC) and EDXRF

No.	Sample no. and location		Sulfate ion, mg/L						$\frac{C_{av}^{EDXRF}}{C_{av}^{IC}}$
			IC technique	EDXRF technique					
			$C_{av}$	$n$	$C_{min}$	$C_{max}$	$C_{av}$	$\sigma$	
1	Balashikha Urban District	B-1	125	6	122	126	123	2	1.0
2		B-2	113	4	112	115	114	1	1.0
3		B-3	89	5	86	89	87	1	1.0
4		B-4	78	4	77	78	77	1	1.0
5		B-5	73	6	65	71	68	3	0.9
6		B-5a	70	7	65	71	67	3	1.0
7		B-6	45	6	44	48	46	2	1.0
8		B-7	92	7	91	92	92	1	1.0
9		B-8	27	4	25	29	28	2	1.0
10		B-9	87	4	80	83	82	2	0.9
11		B-9a	125	7	118	122	121	2	1.0
12	Odintsovsky District	OD-1	24	6	27	30	28	1	1.2
13		OD-3	21	5	22	25	24	2	1.1
14		OD-5	38	6	39	41	40	1	1.1
15		OD-6	35	4	38	40	39	1	1.1
16		OD-7	56	6	52	55	54	1	1.0
17		OD-8	31	7	37	41	39	2	1.3
18		OD-9	24	4	27	27	27	0	1.1
19		OD-10	32	5	35	39	37	2	1.2
20		OD-12	25	6	22	27	24	2	1.0
21		OD-13	16	6	16	19	17	1	1.1
22		OD-15	59	4	56	59	58	2	1.0
23		OD-16	16	4	17	19	18	1	1.1
24		OD-17	26	4	24	27	26	2	1.0
25		OD-18	76	6	74	77	75	1	1.0
26		OD-21	32	4	28	31	29	2	0.9
27		OD-24	35	4	36	39	37	2	1.1
28		OD-25	57	6	55	62	58	3	1.0
29		OD-26	56	4	59	65	61	3	1.1
30	OD-27	47	4	40	44	42	1	0.9	
31	OD-28	74	5	68	74	70	2	0.9	
32	OD-30	22	4	20	23	21	1	1.0	
33	Pushkinsky District	P-1	20	3	20	24	22	2	1.1
34		P-2	29	3	27	31	30	2	1.0
35		P-4	17	3	17	19	18	1	1.1
36		P-5	22	3	19	22	21	1	1.0
37		P-6	17	3	17	20	18	1	1.1
38		P-7	20	5	18	21	20	2	1.0
39		P-8	20	5	18	20	20	1	1.0

Table 2. (Contd.)

No.	Sample no. and location		Sulfate ion, mg/L						$\frac{C_{av}^{EDXRF}}{C_{av}^{IC}}$
			IC technique	EDXRF technique					
			$C_{av}$	$n$	$C_{min}$	$C_{max}$	$C_{av}$	$\sigma$	
40		P-9	26	6	25	28	27	1	1.0
41		P-10	23	5	23	25	24	1	1.0
42		P-11	20	4	20	21	20	1	1.0
43		P-12	12	5	11	13	12	1	1.0
44		P-13	21	6	20	23	21	1	1.0
45		P-14	18	4	16	17	16	0	0.9
46		P-15	38	4	35	38	37	2	1.0
47		P-16	33	5	35	38	37	1	1.1
48		P-17	49	6	47	52	48	2	1.0
49		P-18	22	4	22	23	23	0	1.0
50		P-20	48	5	48	49	49	0	1.0
51		P-21	75	3	80	84	82	2	1.1
52		P-23	45	3	44	45	44	1	1.0
53		P-25	38	4	34	39	36	2	0.9
54		P-27	27	7	27	32	30	2	1.1
55		P-29	16	3	15	17	16	1	1.0
56		P-30	55	3	52	54	53	1	1.0
57		P-31	36	3	38	39	38	1	1.1
58		P-32	30	6	31	33	32	1	1.1
59		P-33	28	5	29	31	30	1	1.1
60		P-34	49	5	46	50	48	2	1.0
61	New Moscow	T-1	29	3	25	26	25	1	0.9
62		T-2	30	5	29	32	31	1	1.0
63		T-3	22	4	21	23	22	1	1.0
64		T-4	38	4	35	38	36	1	0.9
65		T-5	11	5	10	11	10	1	0.9
66		PD-1	55	4	58	61	60	2	1.1
67		PD-2	32	5	29	32	30	1	0.9
68		PD-3	59	5	56	63	59	4	1.0
69		PD-4	59	4	54	57	56	2	0.9
70		PD-5	81	4	77	82	80	2	1.0
71		DM-1	22	5	18	20	19	1	0.9
72		MZh-1	67	4	68	73	71	2	1.1

$C_{min}$ ,  $C_{max}$ , and  $C_{av}$  are minimum, maximum, and average concentrations, respectively (by the data of  $n$  EDXRF measurements); and  $\sigma$  is standard deviation for a data set.

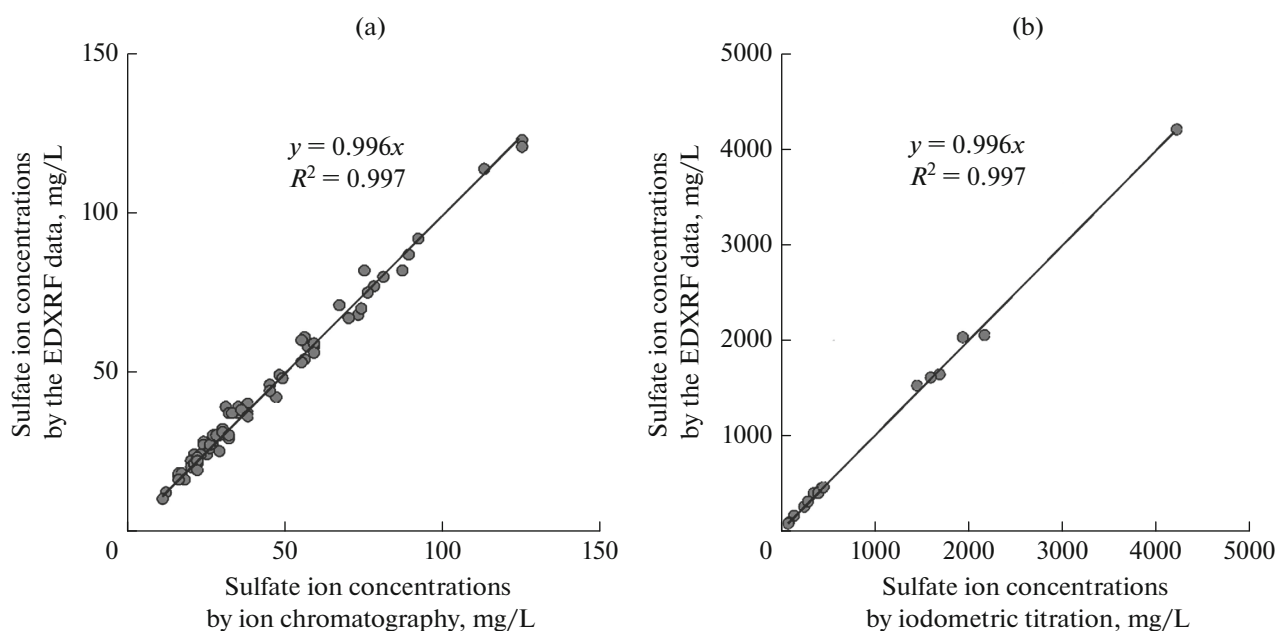
**Table 3.** The results of sulfate ion determination in the waters of watercourses of the ore field area using the techniques of iodometric titration (Titre) and EDXRF

No.	Sample no. and location		Sulfate ion, mg/L						$\frac{C_{av}^{EDXRF}}{C_{av}^{Titre}}$
			Titre		EDXRF				
			$C_{av}$	$n$	$C_{min}$	$C_{max}$	$C_{av}$	$\sigma$	
1	Watercourses draining copper stockworks and near-ore haloes	SN-1	349	3	388	394	392	3	1.1
2		SN-2	432	3	443	446	445	2	1.0
3		CH-3	247	3	251	256	253	3	1.0
4		CH-5*	4226	3	4091	4303	4204	107	1.0
5		CH-8	289	3	301	310	306	5	1.1
6		CH-9	139	3	158	162	159	2	1.1
7		CH-10	83	3	85	88	86	2	1.0
8		CH-18	77	3	73	78	76	2	1.0
9		CH-21	398	3	391	400	396	4	1.0
10		CH-22	453	3	450	458	455	4	1.0
11	Watercourses draining epithermal Au–Ag-mineralization	CH-4*	1941	3	1976	2059	2026	44	1.0
12		CH-6*	1693	3	1623	1653	1640	16	1.0
13		CH-7*	1454	3	1461	1557	1519	51	1.0
14		CH-23*	2174	5	1995	2129	2049	52	0.9
15		CH-24*	1597	6	1545	1700	1604	68	1.0

$C_{min}$ ,  $C_{max}$ , and  $C_{av}$  are minimum, maximum, and average concentrations, respectively (by the data of  $n$  EDXRF measurements); and  $\sigma$  is standard deviation for a data set; \* the samples were tested after preliminary dilution.

samples formerly tested by ion chromatography. The difference between the concentration values is 30% or less (Table 3).

The evaluation of the reproducibility of the data for sulfate ion determination in water using the EDXRF and certified techniques within different concentra-



**Fig. 3.** The reproducibility of the results of sulfate ion determination in water using the EDXRF technique and other analytical procedures: a, springs, ion chromatography,  $n = 72$  and b, watercourses of the ore field area, iodometric titration,  $n = 15$ .



**Table 4.** The reproducibility of the results of sulfate ion determination in water using the EDXRF technique and certified procedures for different ranges of concentration

Ranges of sulfate ion concentrations, mg/L	EDXRF–IC		EDXRF–Titre	
	$n$	$\sigma_r^{\text{rep}}, \%$	$n$	$\sigma_r^{\text{rep}}, \%$
<50	50	6	—	—
50–200	22	3	3	8
200–1000	—	—	6	4
1000–5000	—	—	6	2

$n$  is a number of tested samples;  $\sigma_r^{\text{rep}}$  is relative mean-square deviation by the data of two measurements in  $n$  samples using different procedure; the dash means “no data.”

tion ranges is presented in Table 4. According to the results we obtained, the relative divergences of sulfate ion concentrations by the EDXRF data and those of ion chromatography or iodometry are comparable with the value of a random error of the anion determination using the proposed procedure (2–8%).

## CONCLUSIONS

The proposed technique of X-ray fluorescence analysis for sulfates in aqueous solutions with preliminary concentration by the dried-drop procedure using a portable spectrometer allow one to obtain reproducible results within a wide range of anion concentrations with retention of linearity and stability of a calibrating set.

The verification of the procedure using the results of water sample testing by ion chromatography and iodometric titration shows that relative divergence between the values of sulfate ion concentrations obtained by the EDXRF and certified techniques are comparable to the value of the random error of the anion determination using the proposed procedure (below 10%). In view of the easy sample preparation, low cost of expendables, express mode of measurements, and wide usage of portable spectrometers in geology and allied domains, the technique is very applicable to the analysis of aqueous solutions of various compositions, including the conditions of field laboratories.

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## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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