

A New Method for the Quantitative Determination of Sulfate Ions in Aqueous Extracts from Soils and in Aqueous Media, and Analytical Equipment for Its Implementation

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Abstract: A method and the necessary analytical equipment for the mass quantitative determination of sulfate ions in aqueous extracts from soils and in aqueous media is proposed, consisting in the fact that a known amount of 2-aqueous barium chloride with hydrogen chloride is added to the aliquot of the analyzed sample in the form of an aqueous solution. The resulting insoluble barium sulfate compound reduces the initial concentration of barium chloride. The amount of barium chloride remaining in the solution is determined on the specially designed flame spectrophotometric analyzer. This allows you to calculate the amount of sulfate ions associated with barium, which is automatically performed by the device program. The range of reliably determined concentrations of sulfate ions by the proposed method in water samples ranged from 10 to 100 mg/dm³. The range of reliably determined concentrations of sulfate ions in aqueous extracts from soils ranged from 0.2 to 2.4 C_(1/2SO₄) mol/dm³ (from 10 to 115 mg/dm³). Higher concentrations of sulfate ions must be diluted multiple times with distilled water. The method makes it possible to determine the concentration of sulfate ions in aqueous soil extracts, freshwater reservoirs and rivers, underground sources, tap water, sediments contaminated with sulfuric acid emissions from industrial enterprises. The method is quite simple, accurate and productive. The method is certified by the State Ural Research Institute of Metrology (MVI-66373620-007-2018) and approved by the Federal Agency for technical regulation and Metrology (Rosstandart), as a standard method under No. 253.0080/RA. RU.311866/2019. Patent No. 2681855 of the Russian Federal Service for Intellectual Property with priority dated September 15, 2017 was obtained for the method for determining sulfur in the form of a sulfate ion in an aqueous extract from soils and the equipment necessary for this. Detailed methods for determining sulfate ions in these objects are published in the open press in the book: "Determination of agrochemical and chemical parameters of soils, plants and aquatic environments using flow-decade analysis technology" edited by Academician of the Russian Academy of Sciences R. F. Baibekov.

Keywords: Sulfate Ions, Chemical Analysis, Water Extracts, Soil, Water Samples, Flame Spectrophotometry, Flow-Decade Analysis Technology

1. Introduction

The quantitative determination of sulfate ions in aquatic environments is necessary for assessing the quality of drinking water, assessing the quality of underground sources, and assessing the supply of plants with the specified sulfur compound in the soil. In addition, determining the amount of

sulfate ions in the soil is necessary to control the salinity of land with sulfates in certain regions, as well as to control the content of sulfate ions in acid precipitation, gas emissions from industrial enterprises, and in other cases requiring the determination of sulfate ions. in the aquatic environment (for example, when drilling wells).

Among the studies devoted to the determination of various forms of sulfur in soil and plants, one can mention the work

of Aydinyan R. Kh with co-authors [1]. Their studies were subsequently introduced into GOST 26426-85 [2] as a gravimetric method for determining the sulfate ion in saline soil.

Officially approved methods for the determination of sulfate ions in water are given in GOST 31940-2012 [3]. It describes the determination of sulfate ions by three methods: using Trilon B titrimetry (method 1), using barium chloride titrimetry (method 2), and using barium chloride turbidimetry (method 3).

In the case of the first method, sulfate ions are quantitatively precipitated with barium chloride. To eliminate the effect of carbonates, the sample is acidified with hydrochloric acid. The resulting precipitate of barium sulfate is washed from the rest of barium chloride and dissolved in an ammonia solution with disodium salt of ethylenediaminetetraacetic acid (trilon B). The latter binds the dissolved barium, and the remaining Trilon B is titrated with a solution of chloride or magnesium sulfate with the indicator Eriochrome black T. Based on the results of the titration, the amount of barium associated with Trilon B is determined, and, accordingly, the amount of sulfates in the test volume. The interfering effect of suspended and colloidal substances must be eliminated by preliminary filtration of the sample, and to remove colored substances, the water sample must be passed through an activated carbon column. The interfering effect of cations is eliminated by treatment with cation exchangers. The method is painstaking and does not have high performance.

In the case of using the second method for the quantitative determination of sulfate ions, the prepared sample is titrated with a solution of barium chloride. Barium ions bind sulfate ions, forming a poorly soluble precipitate of barium sulfate. At the equivalence point, an excess of barium ions reacts with an indicator (nitchromazo, chlorophosphonazo or orthonyl K) to form a complex compound, and the violet color changes to blue. According to the amount used for barium chloride titration, the amount of sulfate ion in the sample is calculated. In this method, hydrochloric acid is not used to eliminate the effect of carbonates and other cations on the analysis results, but the water sample is carefully treated with KU-2 cation exchanger. To reduce the solubility of the barium sulfate precipitate, titration is carried out in a water-alcohol or water-acetone medium. The interfering effect of suspended and colloidal substances is eliminated by preliminary filtration of the water sample. To remove colored substances, a water sample is passed through an activated carbon column. All this complicates the analysis and reduces the performance of the method.

A third method for determining the sulfate ion in water uses barium chloride turbidimetry. The method is based on measuring the intensity of turbidity of a water sample containing sulfate ions when interacting with barium chloride. To stabilize the resulting suspension, ethylene glycol is introduced into the reaction mixture, and to reduce solubility of ethyl alcohol. Samples stained with humic compounds are treated with activated carbon. The interfering

effect of suspended and colloidal substances is eliminated by preliminary filtration of the sample through a membrane filter with a pore diameter of $0.45\ \mu\text{m}$. The measurement of optical density is carried out in a cuvette with a base of 20 mm at a spectral wavelength of $364 \pm 20\ \text{nm}$. This method also requires careful preparation of the sample for analysis, and sufficiently accurate measurement of optical density in the short-wavelength region of the spectrum is not always provided by conventional spectrophotometers.

As mentioned above, the officially approved method in Russia for the determination of sulfate ion in soil is GOST 26426-85 [2]. It describes two methods for the determination of sulfate ions in aqueous extracts from saline soils: 1 - weight determination of sulfate ions and 2 - turbidimetric determination of sulfate ions.

In the first case, the essence of the method is the binding and precipitation of the sulfate ion with a solution of barium chloride. To prevent precipitation of carbonates, barium phosphate and other compounds, the solution is acidified with hydrochloric acid. The precipitate of barium sulfate is separated by filtration and washed thoroughly with distilled water. Then it is dried, calcined and the residue is weighed. The preparation of the selected sample for analysis from interfering impurities is rather painstaking, complex and inefficient. For a reliable determination of the sulfate ion, a sufficient amount is required for weighing on a laboratory scale of the 2nd accuracy class with the highest weighing limit of 200 g.

The second method uses a turbidimetric determination of the sulfate ion, similar to that described above. The difference lies in the amount of sulfate ion in the calibration solutions used in the analysis for soils saline with sulfates. To stabilize the suspension, glycerin or polyvinyl alcohol is used instead of the more toxic ethylene glycol. For photometry, a spectral wavelength of 520 nm is used, which is more convenient.

Among the significant disadvantages of the turbidimetric determination of the sulfate ion is the contamination of the internal surfaces of the glass of the cuvettes by the precipitate of barium sulfate. They are periodically required to be cleaned using Trilon B. In addition, this method does not allow direct analysis of soil extracts stained with humic compounds, which complicates and slows down the analysis.

The aim of this work was to develop a new method for the quantitative determination of sulfate ions in aqueous media and in water extracts from soils using modern spectral analytical equipment.

Teams of specialists from KINZH-AGRO LLC and AGRONET LLC conducted research and proposed a new universal method, analytical equipment and a flame photometer for the quantitative determination of sulfate ions in water extracts from soils, freshwater reservoirs and rivers, underground sources, tap water, precipitation contaminated with sulfuric acid emissions from industrial enterprises. The method is productive, quite simple and has no drawbacks in the above methods.

2. Research Methodology and Technical Solutions

The essence of the proposed method for the analysis of water extract from soils for the quantitative determination of sulfate ions was as follows. To an aliquot (50 or 100 cm³) taken from the aqueous soil extract, an exact volume of a solution of 2-aqueous barium chloride of a known concentration was added, which bound sulfate ions into an insoluble compound of barium sulfate. This led to a decrease in the amount of soluble barium added to the soil extract. The decrease in the amount of soluble barium was determined by the flame photometric method on a specially designed spectrophotometric analyzer. Preliminarily, the device was calibrated using solutions of a calibration scale with known concentrations of sulfate ions. The amount of bound sulfate ion in the tested samples was calculated by comparing the obtained results with the data of the analysis of calibration solutions. The obtained results were processed by the device's microprocessor program according to a specially developed algorithm.

The effect of carbonates, which also react with sulfate ion to form sulfate compounds that are slightly soluble in water, for example, calcium sulfate, was leveled by adding diluted hydrochloric acid to the soil extract, in which they are easily soluble. At the same time, the influence of the concentration of hydrochloric acid on the solubility of barium sulphate, which is formed during the reaction with sulfate ions of soil extract, was studied.

It turned out that an increase in the concentration of hydrochloric acid by more than two times in solutions for the precipitation of sulfate ions specified in GOST 26426-85 (60 cm³ of hydrochloric acid with a concentration of 1 mol/dm³ in a volume of 1 liter) does not significantly affect the results of the analysis. Thus, the solubility of one gram of barium in the BaSO₄ compound (1.7 g) in this case was only about seven milligrams, which is included in the measurement error. However, an increase in the concentration of hydrochloric acid makes it possible to reliably level the effect of carbonates, primarily calcium sulfate, on the results of measurements of the concentration of sulfate ions in aqueous soil extracts and aqueous media.

The quantitative content of sulfate ions in aqueous media was studied in a similar way.

The flame spectrum analyzer developed for this method

(Figure 1) ensured the measurement of the radiation intensity of the barium hydroxide molecular band in the near infrared region at a spectral wavelength of 870 nm using a propane-air burner flame [6].

The design of the proposed spectrum analyzer included a gas-air system with gas flow control valves, a propane burner for excitation of barium optical radiation, a spectrophotometer with a diffraction grating for detecting and recording barium emission lines, a microprocessor with software for controlling the device components and processing measurement results. To improve the accuracy of determining the concentrations of sulfate ions, the software of the device allowed automatic correction of the measurement results in the course of operation according to the selected control solution of the calibration scale.

Due to the relatively not very high temperature of the propane-air flame, the barium line intensities in the required concentration range are also not high. Therefore, the design of the device made it possible, if necessary, to amplify the signal of the photodetector up to 500 times.

In the process of flame photometric studies, the influence of alkali and alkaline earth elements on the measurement of barium was evaluated. First of all, attention was paid to the elements sodium and potassium, which are always present in the soil and in natural waters. Among the spectral emission lines of sodium, as close as possible to the spectral emission line of barium (870 nm), which was chosen for measurements, is the line at 819.5 nm. For potassium this line is 769.9 nm, for rubidium 794.8 nm, for cesium 894.4 nm. The last two elements are very little present in the analyzed samples of water and soil, and therefore practically do not affect the measurement of barium. The conducted studies have shown that with a low sensitivity of the device, but sufficient to determine the initial used concentration of barium, the concentration of potassium up to 0.5 mol/dm³ does not affect the measurement of barium. At a potassium concentration of 1.0 mol/dm³, the error in determining barium is only + 0.8%, i.e. very insignificant. These concentrations of potassium are very rare in ordinary soils and natural waters. Similar results were obtained for sodium.

The presence in the analyzed samples of the main alkaline earth elements (magnesium, calcium, strontium) does not interfere with the determination of barium, since the spectral emission lines of these elements are in other spectral ranges.

Table 1. Effect of a barium sulfate suspension introduced into a propane-air burner flame on radiation in the spectral range used.

Number in sequence	Graduating scale of sulfate ion, mmol/dm ³	Pure solution measurement (results of A/D Converter) Sample X	Measurement of a solution with a suspension of barium sulfate (results of A/D Converter). Sample Y
1	0.00	14416	13934
2	0.20	13570	13163
3	0.40	12102	12004
4	0.80	9464	9373
5	1.20	6905	6905
6	1.60	4126	4396
7	2.00	1836	1826
8	2.40	75	81

Note. The results of the regression analysis of the data in Table 1 (performed by MS Excel): multiple R, 0.999575; R square, 0.99915; normalized R square, 0.999008; standard error, 165.38; number of observations, 8.

In the process of research, the concentrations of barium chloride were selected that do not clog the atomizer when the aerosol is fed into the burner flame. It was also found that the ingress of a suspension with a precipitate of barium sulfate into the burner flame does not increase the radiation intensity in the above spectral range and does not introduce a significant error in the determination of sulfate ions (Table 1). This is due to the insufficiently high temperature of the propane-air flame of the burner to ionize the barium sulfate compound. However, the ingress of barium sulfate sediment into the atomizer and burner leads to its mechanical deposition on their inner walls, clogs the atomizer nozzle and distorts the analysis results.

3. Experimental Studies and Results

To assess the reproducibility and correctness of the proposed method for determining sulfate ions in aqueous extracts from soils and in aqueous media, an arbitration method was chosen based on the turbidimetric determination of the concentration of sulfate ions (GOST 26426-85 for soil analysis and GOST 31940-2012 for the analysis of aquatic environments). The choice of turbidimetric methods for the analysis of sulfates is due to the fact that they provide a fairly high performance, which is very important for large volumes of analytical work. In addition, they are less complex than other sulfate ion analysis methods and are metrologically validated.

Due to the fact that GOST 26426-85 prescribes the determination of sulfate ions in water extract from saline soils, and in the present work, ordinary soils of various types were also studied, the calibration of the instrument (KFK 3-01) for turbidimetric analysis was carried out on a scale with sulfate concentration -ions 10 times less than in the specified

normative document. In order to accurately measure small concentrations of sulfate ions by the turbidimetric method, a telescopic attachment for a Z-shaped flow cell with a base of 30 mm was built into the KFK 3-01 colorimeter, which was automatically filled with the analyzed sample using a non-pressure peristaltic pump NPM-4, see [7], pp. 58-68. This made it possible to quickly fill the cuvette with a sample and wash it with distilled water, with control of the base signal when measuring the optical density of distilled water.

During two years of research and development of a new method for the quantitative analysis of sulfates, more than 14 types of soils, both arable and sub-arable horizons, and 15 water sources were investigated. In the latter case, for example, it turned out that the content of sulfate ions in precipitation in the form of snow on a lawn near the Third Ring Road (the area of Maryina Roshcha, north-east of Moscow) with heavy traffic is not high and amounts to 7.5 mg/dm³. And a sample of snow on the experimental field of the RGAU-MSHA them. K. A. Timiryazev (near the Experimental Station, Pryanishnikov St., Moscow) does not actually contain sulfate ions, only traces.

The main tests of soil samples for the quantitative content of sulfate - ions in the water extract and in water samples for metrological evaluation of the results were carried out within a month and included three cycles of measurements. In each cycle, each individual sample was analyzed in triplicate (three samples from one soil sample or three water samples). When analyzing soils, each obtained extract from individual samples was simultaneously analyzed by new flame photometric and standard turbidimetric methods. All extracts from each cycle were repeatedly analyzed for several days and preserved in a refrigerator until the next cycle of measurements.

Table 2. Determination of the content of sulfate ions in water extracts from soils by flame photometric and turbidimetric methods.

Number in sequence	Name of soil samples	Flame photometric measurement C(1/2SO ₄) mmol/dm ³			Turbidimetric measurement of C(1/2SO ₄) mmol/dm ³			Student's criterion, t-test
		Mean X	Standard deviation.	Coefficient of variations %	Mean X	Standard deviation.	Coefficient of variations %	
1	2	3	4	5	6	7	8	9
1	Standard sample No. 30901. Brown heavy loam solonetz	1.34	0.043	3	1.51	0.120	8	1.577E-07
2	Standard sample No. 31002. Chernozem heavy loam solonetz	1.42	0.047	3	2.51	0.611	24	2.455E-07
3	Sample No. 36601. Meadow-chestnut solonetzic-saline soil	5.37	0.716	13	7.02	1.048	15	4.970E-05
4	Hydromorphic solonchak from the Soil Museum of the Timiryazev Agricultural Academy. Horizon 21 - 40 cm	19.7	1.78	9	21.1	1.34	6	0.055
5	Solonchak hydromorphic from the Volgograd region. Soil Museum of the Timiryazv Agricultural Academy. Horizon 0 - 10 cm	14.6	0.167	1	15.6	0.81	5	0.813
6	Solonchak hydromorphic from the Volgograd region. Soil Museum of the Timiryazv Agricultural Academy. Horizon 10 - 30 cm	7.1	0.312	4	8.4	1.68	20	0.036
7	Solonchak hydromorphic from the Volgograd region. Soil Museum of the Timiryazv Agricultural Academy. Horizon 30 - 50 cm	5.0	0.795	16	6.25	1.59	25	0.039

Note 1. In Table 2, samples No. 2 and No. 3 are stained brown with organic compounds and overestimate the results of turbidimetric measurements.

Note 2. Statistical processing of the results of the analysis of this and in the following table 3 was performed by MS Excel.

Table 2 presents the results of the analysis of the sulfate ion in the water extract from soils by two methods: the proposed flame photometric method and the standard turbidimetric method. The data given in the table show that the analysis of sulfate ions by the indicated methods gave fairly close results for almost all tested samples. Samples No. 1 and No. 2 gave better results for the analysis of sulfate ions by the turbidimetric method compared to the flame photometric method. This is due to the coloration of these soil extracts with humic compounds.

The correlation coefficient of the two samples of measurement results was 0.998 (close to 1). Student's t-test is given in the tables. However, the coefficient of variation for

the flame photometric method is, on average, two times less than for the turbidimetric method (7% and 14%). These data indicate a better reproducibility of the results of measuring the concentration of sulfate ions in water extracts from soils by the flame photometric method in comparison with the turbidimetric method.

According to the structure of testing soil samples for the quantitative content of sulfate ions in the water extract described above, analyzes for the content of sulfate ions in samples of water sources were similarly carried out.

Table 3 shows the results of the analysis of the sulfate ion in water of natural origin by flame photometric and turbidimetric methods.

Table 3. Determination of the concentration of sulfate ions in water samples by flame photometric and turbidimetric methods.

Number in sequence	Name of water samples	Flame photometric measurement, mg/dm ³			Turbidimetric measurement mg/dm ³			Student's criterion, t-test
		Mean X	Standard deviation.	Coefficient of variations %	Mean X	Standard deviation.	Coefficient of variations %	
1	2	3	4	5	6	7	8	9
1	A sample from a borehole of the "Mirny" gardening association. Moscow region, Istra district. 06/11/2018.	22.5	1.21	5	25.8	5.92	23	0.571
2	A sample from the Bolshoi Timiryazevsky Pond near the spillway. Timiryazev Academy area. 06/18/2018.	17.1	1.58	9	18.9	3.57	19	0.446
3	A sample from the Moskva River near the Crocus City Exhibition Center. 06/12/2018.	18.9	2.35	12	19.4	3.68	19	0.735
4	A sample of cold tap water at the Department of Radiology TSCA. 06/25/18.	28.7	1.06	4	32.2	5.04	16	0.052
5	Sample from the Moskva River in the Rublyovka area on June 23, 2018.	19.8	1.37	7	20.2	3.73	18	0.812
6	Sample from the Small Pond. Krylatsky district, Moscow.	16.2	0.88	5	15.9	0.88	6	0.625
7	Sample from the Big Pond. Krylatsky district, Moscow.	22.1	0.36	2	20.4	1.70	8	0.149
8	Sample from the Likino-Dulyovo well. Moscow region.	6.3	0.20	3	5.9	1.68	28	0.702
9	Sample from the source "Holy Spring". Park Krylatsky hills, Moscow	50.0	0.25	13	47.0	5.59	12	0.395
10	Sample from the source "Lower Spring". Park Krylatsky hills, Moscow.	100.0	1.61	2	95.5	6.17	6	0.268
11	Sample from the Likino-Dulyovo core. Moscow region.	60.2	2.53	4	54.7	6.22	11	0.197

Note. Student's criterion (t-test) shows that the difference in the results of the analysis of sulfate ions obtained by two methods is not significant: t-test > 0.05.

Analysis of water samples for this indicator by two methods showed similar results.

In this case, the reproducibility of the analysis when determining the amount of sulfate ions by the flame photometric method is also better than the turbidimetric method. The coefficient of variation for the flame photometric method in the quantitative analysis of sulfate ions in aqueous media is, on average, 2.5 times lower than for the turbidimetric method (6% and 15%).

The proposed flame photometric method for the quantitative determination of sulfate ions in aquatic environments and analytical equipment for implementation make it possible to organize mass surveys of soils for

agricultural and industrial use, as well as water resources for this indicator.

Technology of Mass Analyzes for the Quantitative Determination of Sulfate Ions in Water Extracts from Soils and in Water Samples by Flame Photometric Method.

The proposed technique makes it possible to organize a continuous-decade technology for determining the sulfate ion in water extracts from soils during mass surveys of land for this indicator, similar to the technology for analyzing phosphorus and potassium or organic matter in soil [4, 5]. In this case, the sequence of technological operations for the analysis of sulfate ions is as follows.

A sample of air-dry soil is placed in the container of the

KBM technological cassette (Figure 2). A certain volume of distilled water degassed by boiling is added with a single-position Klychnikov dispenser (Figure 3) or a 10-position dispenser DZh-10 (Figure 4). The containers are hermetically sealed and agitated to extract sulfates using a BB-1 agitator (Figure 5) or similar.

The resulting suspension for separation and obtaining a liquid fraction is centrifuged (Figure 6), or filtered (Figure 7) through a paper filter. An aliquot is taken from the obtained liquid fraction with a DOAZh-10 dispenser (Figure 8), transferred to another KMM technological cassette, and the required volume of a solution of 2-aqueous barium chloride of the required concentration is added, which ensures the binding of the entire amount of sulfate in the sample and guarantees the presence of the remainder of the initial solution barium, not associated with sulfates.

The liquid fraction obtained from the suspension of barium sulphate is separated from the precipitate by centrifugation or filtration, or by settling the suspension. The concentration of the remaining barium in the solution, not associated with sulfates, is determined by the flame photometric method (Figure 1). The quantitative content of sulfur in the form of sulfate ion is calculated from the difference between the initial amount of added barium and its residue in the analyzed solution (Figure 10). The analysis results are processed automatically according to the algorithm of the device program.

Determination of sulfate ion in natural waters is carried out in the same way as in the analysis of soil extracts, excluding operations to obtain an extract from soils. The water sample, if necessary, is purified from mechanical impurities by filtration, an aliquot is taken, and all further analytical and technological operations described above are performed.

The proposed technology makes it possible to analyze at least 200 or more soil or water samples per day.



Figure 1. Sulfate Flame Spectrum Analyzer.

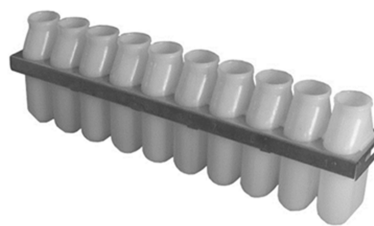


Figure 2. Ten-position KBM cassette for placing soil samples, water doses and shaking on a shaker.



Figure 3. Klychnikov's one-position manual dispenser. On the left is a separate dispenser, on the right is an assembly.

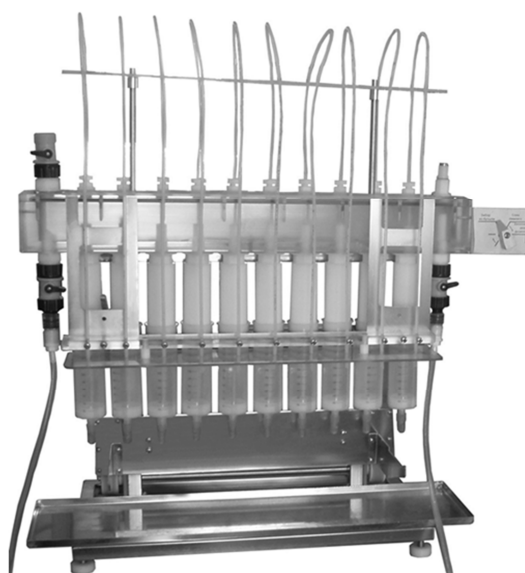


Figure 4. Ten-position dispenser DZh-10 for dispensing water into the container of the KBM cassette. It is used instead of the Klychnikov dispenser if it is necessary to increase the productivity of analytical work.

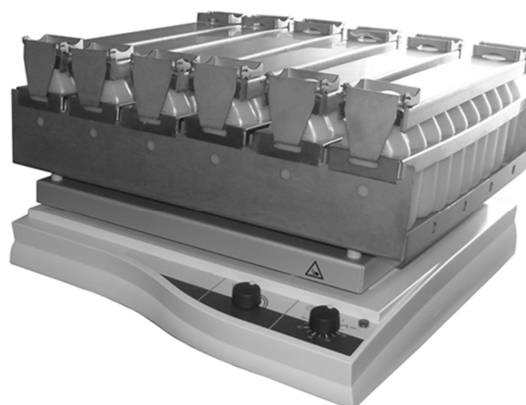


Figure 5. Cassette shaker KBM for extraction of sulfates from the soil.



Figure 6. Centrifuge Ts-2000 for separation of solid and liquid fractions of soil suspensions. On the left is a general view, on the right is a cassette loading chamber.

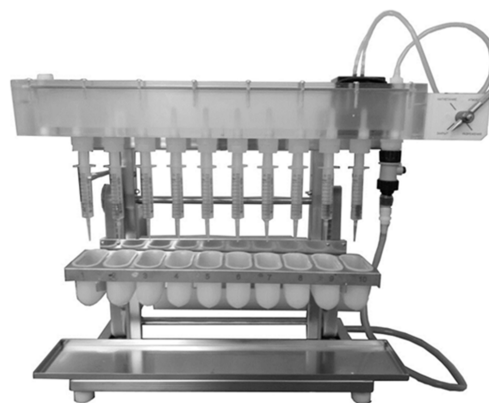


Figure 8. Ten-position dispenser-selector DOAZH-10 for sampling liquid above the sediment after centrifugation or after filtration.



Figure 7. Filter unit BFM-2 for filtering soil suspension from KBM cassettes into KMM cassettes.



Figure 9. Dosing device for dosing barium chloride solution into selected doses of soil extract.



Figure 10. Calibration plot of the dependence of the quantitative content of barium (Y-axis) on the concentration of sulfates in solution (X-axis). Relative values.

4. Conclusions

A new method and equipment for the flame photometric determination of the amount of sulfate ions in aquatic environments: soil extracts, natural waters, sediments and other objects is proposed. The error in determining this indicator in the analysis of soil extracts ranged from 3 to 16%. The error in determining this indicator in the analysis of aqueous media ranged from 3 to 13%.

The proposed method and analytical equipment can be used in the flow-decade technology for the analysis of this indicator during mass surveys of soil and natural aquatic environments.

The described in-line technology for the determination of sulfates in aqueous media is widely used in the agrochemical service of Russia for the analysis of many indicators [8]. A detailed description of the techniques using this technology is described in a monograph published in Russia in 2021 [9]. Currently, these methods and technology are approved in Russia as standards for soil analyses for chemical indicators, for example, for the analysis of phosphorus and potassium in carbon-ammonium extract from soils [10], for the analysis of soil acidity [11], for the analysis of phosphorus and potassium in hydrochloric acid extract from soils [12], for the analysis of sulfates in water extraction from soils [13].

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