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Determination of Arsenic in Rocks and Soils Using Photometry

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Abstract

Optimal parameters for determining As by the photometric method have been established. Results of arsenic determination in rocks and soils by means of photometry are presented. This method is distinguished by the low detection limit (0.1 g/t) and economic efficiency in comparison with other modern analytical methods (atomic absorption spectrometry, atomic emission spectrometry with inductively coupled plasma, and mass spectrometry with inductively coupled plasma). For rocks and soils containing organic matter, the applicability of the existing methods of acid decomposition and melting was evaluated. The results of As determination by means of photometry were compared with its certified contents in the State Standard Samples of rocks (SGKhM-1, SGKhM-3, SG-3, SZR-2, SKD-1, SGKh-1), and with the data obtained by means of mass spectrometry with inductively coupled plasma on volcanoclastic greywacke. The parameters of As determination by means of photometry were optimized. It is recommended to use the photometric method for mass determination of arsenic in rocks and soils.

Keywords: arsenic, arsine, arsenic molybdenum blue, rocks, soils, photometric method

INTRODUCTION

At present, much attention is attracted to the determination of heavy metals in various environmental objects, because environmental pollution resulting from human activities is intensively increasing [1, 2]. One of the main reasons for technogenic soil pollution, especially over urban and adjacent territories, is the income of heavy metals, as well as non-metals, in particular arsenic (As). Arsenic is a carcinogenic chemical element assigned to the class of extremely dangerous substances, while it is a rather mobile element, able to migrate with water and to be absorbed by plants [3, 4]. For this reason, determination of arsenic in soil is an urgent problem. The maximum permissible concentration (MPC) of this element in drinking water is 0.01 mg/L according to GN 2.1.5.1315-03. The average background As content in natural soil is 6 g/t [5], and its clarke in urban soil is 15.9 g/t [6], which is 3–8 times higher than the MPC for soil (2 g/t).

Many methods are used to determine As content in rocks and soils; the most sensitive ones are presented in Table 1. However, all of them have definite disadvantages. The major limitations for the wide application of precise mass spectrometry [14] and atomic emission [12] with inductively coupled plasma (ICP-MS and ICP-AES, respectively) are very high cost of the equipment and the services. In addition, to determine As with the help of these methods and atomic absorption spectroscopy (AAS) [15], it is necessary to use an attachment of hydride generation,

TABLE 1

Methods of arsenic determination in rocks and soils

Method	Detection limit, g/t	Reference
Photometry:		
As isolation with sodium hypophosphite after co-precipitation with iron (III) hydroxide	50	[7]
with molybdenum blue after extraction in the form of iodide complex	10	[8]
with arsenic molybdenum / antimony-arsenic molybdenum blue after distillation in the form of AsH_3	0.1	[9]
Colorimetry using Gutzeit method	4	[10]
XFA in combination with extraction and sorption on cellulose	15	[11]
AAS in combination with hydride generation	0.1	[12]
Polarography in combination with As distillation in the form of trichloride	10	[13]
ICP-MS	0.1	[14]
ICP-AES	0.05	[12]

Note. XFA is X-ray fluorescence analysis; AAS is atomic absorption spectroscopy; ICP-MS and ICP-AES are mass spectrometry and atomic emission spectrometry with inductively coupled plasma, respectively.

which allows As separation from interfering elements [14, 16]. However, such an attachment is not always available at analytical laboratories because of its high cost and a very narrow range of hydride-forming elements to be determined using it. Besides, ICP-MS and ICP-AES require rock decomposition with different acids, which may result in the formation of readily volatile As-containing compounds and thus lead to underestimated As concentration [17].

A disadvantage of X-ray fluorescence analysis (XFA) is the interfering analytical line of Pb Lα1, which is superimposed on the analytical line of As Kα1 [11]. In the case of noticeable Pb content in rocks, it is necessary to measure As using other lines, which worsens the accuracy of measurement and causes an increase in the detection limit.

The most widely used procedures are those based on photometric determination of As in rocks and soils [7–9]. They combine high sensitivity, broad range of determined concentrations with rather low analysis prime cost.

Photometric determination of As employs the ability of the element to form coloured heteropolyacids [18]. In some cases, the optical density of the solution of arsenic molybdenum blue is measured [9, 18]. However, the conditions of sample preparation for photometric analysis that are described in the literature differ from each other [9, 19, 20]. These conditions include the choice of reagents used during sample decomposition, as well as the conditions for the separation of the element to be determined. The known decomposition methods do not always take into account the composition of the substance under analysis, which frequently leads to underestimated results and requires choosing a suitable method.

Sample preparation for analysis is to provide complete extraction of the element and its transformation into the soluble form without any losses. In the majority of known procedures for As determination in rocks and soils, acid decomposition with nitric and sulphuric acids is employed. This mixture is a strong oxidizer; however, this decomposition method is considered to give no positive results if a sample contains organic compounds, mercury-containing minerals, or As is present in scorodite ($FeAsO_4 \cdot 2H_2O$) [7]. To eliminate the losses caused by the presence of organic substances, it is necessary to add oxidizers, for example hydrogen peroxide. To decompose silicate rocks, it is recommended to use hydrogen fluoride in combination with oxidizers. However, it should be taken into account that arsenic may form volatile compounds in the presence of HF and HCl, which is accompanied by the loss of the analyte [17]. For some silicates, especially those

not rich in SiO_2 or aluminosilicates, aqua regia may also be used (HNO_3/HCl = 3 : 1) [21, 22], the reagent that is widely used to dissolve many As-containing minerals, in particular the minerals of safflorite ((Co,Fe)As_2) and skutterudite ((Co,Ni)As_3) groups. These minerals are almost insoluble in other acids [21]. A mixture of HNO_3, H_2SO_4 and $HClO_4$ is frequently used to decompose many rocks and minerals [18].

The present work is based on the procedures described in [7–9], in which rock and soil samples are decomposed using a mixture of HNO_3 and H_2SO_4. Further procedures related to As isolation by distillation in the form of arsine (AsH_3) and the formation of coloured solution of arsenic molybdenum blue for photometric determination are based on the procedure described in [9]. This method is more sensitive in comparison with other spectrophotometric methods [7, 8], because distillation in the form of AsH_3, chosen to separate As from the sample material, allows isolation of As in micro-amounts, and the complex in the solution under photometric analysis is characterized by more intense colouring. To exclude the interfering influence of the matrix, As extraction and co-precipitation with iron (III) hydroxide are less frequently used. The latter methods bring substantial complications into analysis, make it longer, and cause large losses during separation.

The goal of the present work was to improve some conditions of the photometric analysis of arsenic in rocks and soils, specifically, to establish the effect of zinc granule size on distillation time, and to reveal the best method of decomposition for rocks and soils containing organic matter.

EXPERIMENTAL

Reagents graded as chemically pure and pure for analysis, and distilled water were used in the work. *Reagent solution* was prepared from ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), *reducing solution* – from potassium iodide (KI), tin (II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$) and hydrogen chloride (HCl), *spare absorbing solution* – from iodide (I_2) and KI, *working absorbing solution* – from the spare absorbing solution and the solution of sodium hydrocarbonate ($NaHCO_3$). *Working standard solution* with As concentration 100 μg/mL was prepared from sodium hydroarsenate dodecahydrate ($Na_2HAsO_4 \cdot 12H_2O$) or the State Standard Samples (SSS) of arsenic (III) ions. The *working solutions* containing 0, 0.04, 0.1, 0.2, 0.3, 0.4 μg/mL As were prepared directly on the day of application by diluting the solution with As concentration 100 μg/mL.

The optical density of coloured solutions was determined with the help of photoelectric photometer KFK-3-01-ZOMZ (Zagorst Optical-Mechanical Plant, Russia) with the spectral range of 315–990 nm. The correctness of the procedure was evaluated according to the results of the analysis of SSS with certified and approximate As content. In addition, comparative analysis of the results of As determination in the samples of volcanoclastic greywacke by means of photometry and ICP-MS using an X Series 7 mass spectrometer (Termo Electron Corporation, USA) at the Institute for Design Problems in Microelectronics RAS (Chernogolovka, Head of Analytical Group: V. K. Karandashev). Sampling and sample storage were carried out in agreement with GOST 21153.0-75 [23].

Rock samples were decomposed in heat-resistant beakers with clock glass, conical flasks with glass funnels, platinum cups and crucibles. Acid decomposition was performed on an electric stove, and alloying was carried out in a muffle furnace. Separation of As from the sample was achieved using distillation equipment [9], which included a conical flask according to GOST 25336-82 [24], a glass test tube with expansion for cotton wool impregnated with lead (II) acetate, glass tube and a test tube for the absorbing solution. Before using, laboratory vessels were washed with HNO_3 (diluted with H_2O, 1 : 1 by volume), then with distilled water, and dried.

Rock decomposition

The weighted portions of samples were 1.0–2.0 g for As content up to 20 g/t. For As content above 20 g/t, a smaller weighted portion was taken, or a sample was diluted after decomposition, and then an aliquot was taken. Decomposition was carried out using the following acids and mixtures: 1) HNO_3 and H_2SO_4; 2) HNO_3, 10 M H_2SO_4 and HF; 3) a mixture of HCl and HNO_3 (1 : 3 by volume), H_2SO_4 (diluted with H_2O, 1 : 1 by volume); 4) HNO_3, 10 M H_2SO_4 and $HClO_4$; 5) $NaCO_3$ and KNO_3 (1 : 1 by mass); 6) HNO_3, H_2O_2 and H_2SO_4.

Decomposition conditions:

1) A mixture of HNO_3 and H_2SO_4. The weighted portion of the sample was placed in a beaker or a conical flask, then 5 mL of concentrated HNO_3 with 5 mL of concentrated H_2SO_4 were

added, and mixing was carried out. The beaker (flask) was capped with clock glass or a funnel, and slowly heated avoiding rapid reaction. The mixture was boiled until white vapour of sulphur (IV) oxide appeared. If the sample did not lose colour, after cooling, 5 mL of HNO_3 was added, the mixture was capped with the clock glass (funnel) and again boiled until the white vapour appeared. If necessary, the latter operation was repeated. Since HNO_3 hinders subsequent distillation of As, in order to remove nitrogen oxides and HNO_3, 5 mL of water was added into the cooled beaker (flask) by flowing along the walls, and the vessel was heated until white vapour appeared. The operation with water was repeated one more time. Then the solution was cooled and transferred into the flask for distillation.

2) A mixture of HNO_3, H_2SO_4 and HF. The weighted portion of the sample was placed in a platinum cup, then acids were added: 5 mL of concentrated HNO_3, 5 mL of 10 M H_2SO_4 and 25 mL of concentrated HF. The solution was evaporated until dry. The dry residue was crushed and transferred with water into the flask of the distillation set-up.

3) A mixture of HCl and HNO_3 (1 : 3) and H_2SO_4. The weighted portion of the sample was placed in a beaker, then 15 mL of a mixture of HCl and HNO_3 (1 : 3 by volume) was added, kept for 15–20 min, and evaporated to 5 mL. Then 10 mL of H_2SO_4 (diluted with H_2O, 1 : 1 by volume) was added, and the mixture was evaporated until the vapour of H_2SO_4 appeared. Then the mixture was cooled, the beaker walls were washed with water, and again evaporation was carried out until H_2SO_4 vapour appeared. After cooling, the solution was transferred into the flask for As distillation.

4) HNO_3, H_2SO_4 and $HClO_4$. A weighted portion of the sample was placed into the conical flask, 10 mL of concentrated HNO_3 was added, and then the mixture was stirred and heated for 15 min. After cooling, 10 mL of 10 M H_2SO_4 and 7 mL of concentrated $HClO_4$ were added, and then the mixture was evaporated until white vapour appeared. After cooling, 10 mL of 10 M H_2SO_4 was added to the residue and the mixture was evaporated almost until dry. The dry residue was transferred with distilled water into distillation flask.

5) $NaCO_3$ and KNO_3. A mixture of $NaCO_3$ with KNO_3 (1 : 1 by mass) in the amount of 2.5 g was placed in a platinum crucible, the weighted portion of the sample was added, and 0.5 g of the same mixture was added on top after mixing. The crucible was capped with a platinum cap, gradually heated in the muffle furnace to 800 °C, and kept at this temperature for 20–30 min. After cooling, water was added into the crucible, and the mixture was heated until the melt was dissolved. The solution was filtered through a paper filter, the filter was washed, and the filtrate was transferred into a distillation flask.

6) A mixture of HNO_3 and H_2O_2, H_2SO_4. The weighted portion of the sample was placed in a beaker or a conical flask, 5 mL of concentrated HNO_3 was added, then 1 mL of concentrated H_2O_2, mixing was performed, and the mixture was capped with a clock glass. The mixture was boiled until half of it was evaporated. After cooling, 5 mL of HNO_3 and 5 mL of H_2SO_4 were added. After that, decomposition was continued as described in the first of the described methods.

Arsenic separation in the form of arsine

Separation of As in the form of arsine (AsH_3) was performed using a distillation set-up. The solutions obtained after the decomposition of rock and soil samples contain As in the form of H_3AsO_4 (As(V)). With the help of $SnCl_2 \cdot 2H_2O$ in the acid medium, As(V) is reduced to As(III) according to the equation: $H_3AsO_4 + SnCl_2 + 2HCl \rightarrow H_3AsO_3 + SnCl_4 + H_2O$. To remove sulphuric acid that was used during decomposition of a rock or soil sample, KI is added into the solution. The reduction of H_3AsO_3 to AsH_3 is carried out with the help of hydrogen (H_2), formed through the interaction of HCl with zinc (Zn).

Zinc is used as a reducing agent in the form of granules (d = 5–7 mm) or tablets of zinc powder, as well as in the grain form (d = 0.3–1.5 mm). The grained form allows avoiding stormy reaction Zn at the initial period in comparison with the tablets of zinc powder, and to complete distillation within several minutes, while the use of granulated Zn allows As separation within ~60 min.

The solutions obtained after sample decomposition were placed into a distillation flask, and then water was added to reach the volume of 50 mL. Simultaneously, As distillation in reference solutions was carried out. A layer of cotton wool impregnated with lead (II) acetate was put in the expansion on the glass cap to capture hydrogen sulphide, which decreases the efficiency of separation. Reducing solution and metal granulated (d = 5–7 mm) or grained (d = 0.3–1.5 mm) zinc was added into the flask of distillation set-up, the flask was quickly closed with a cork with connective tube, the tube end was immersed into the test tube with the absorbing

solution. Distillation was carried out at room temperature during the time interval determined in the course of experiments. After distillation was over, the tubes with absorbing solution were disconnected from the distillation set-up.

The formation of volatile arsine is described by the equation: $H_3AsO_3 + 3Zn + 6HCl \rightarrow AsH_3\uparrow + 3ZnCl_2 + 3H_2O$. At the moment of evolution, AsH_3 is absorbed by the iodine solution with the formation of arsenate ion (AsO_4^{3-}), which is later on determined by means of photometry in the form of arsenic molybdenum blue.

The formation of arsenic molybdenum blue

A solution of sodium pyrosulphite ($Na_2S_2O_5$) was added into the tubes with the distillate to remove excess iodine, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was added for colouring, and hydrazine sulphate ($N_2H_4 \cdot H_2SO_4$) was added as a reducing agent. The solutions were boiled in a water bath for 10 min and cooled to room temperature.

Measurement of optical density

Photometric measurements were carried out in the cells with the light passage length of 10 mm, with respect to water, at the maximal wavelength. To choose the wavelength, we studied the spectra of arsenic molybdenum blue solutions within wavelength range 820–860 nm.

RESULTS AND DISCUSSION

Optimal conditions for recording the spectra

The spectrum of arsenic molybdenum blue within the infrared range from 820 to 860 nm has an absorption maximum at 841–845 nm. We chose 843 nm as the working wavelength for the quantitative determination of As.

The effect of distillation time and the amount of granulated Zn on AsH_3 distillation

For the complete reduction of As to AsH_3, a definite amount of metal zinc is necessary, along with a definite time of distillation. It is recommended the procedure described in [9] to use 5 g of granulated Zn, which was implemented in the present work. To choose an optimal weight of sample portion, distillation of As solutions with the concentration of 0.4 μg/mL was carried out with the addition of 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 g of granulated Zn. It was determined that the highest optical density was that of the solutions obtained with 5 g Zn (Fig. 1, *a*).

Different recommendations are given in the literature concerning the time of distillation: 1) 45–60 min [9]; 2) not less than 1 h [19]; 3) 18–20 h [20]. We carried out distillation with 5 g of granulated Zn for 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2 h. The optimal distillation time turned out to be 1 h (see Fig. 1, *b*). It is necessary to carry out distillation under strictly identical conditions for all solutions (with the same time and amount of Zn) to avoid divergence in determination.

Effect of distillation time and the amount of grained Zn on AsH_3 distillation

To choose an optimal weighted portion of grained Zn, the same amounts of Zn as those in the experiment with granulated Zn were added into distillation flasks: 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 g. The most complete distillation was determined to proceed with the weighted portion of 3.5 g (see Fig. 1, *a*). The excess and lack of grained Zn caused a decrease in optical density, and thus a decreased result of As determination.

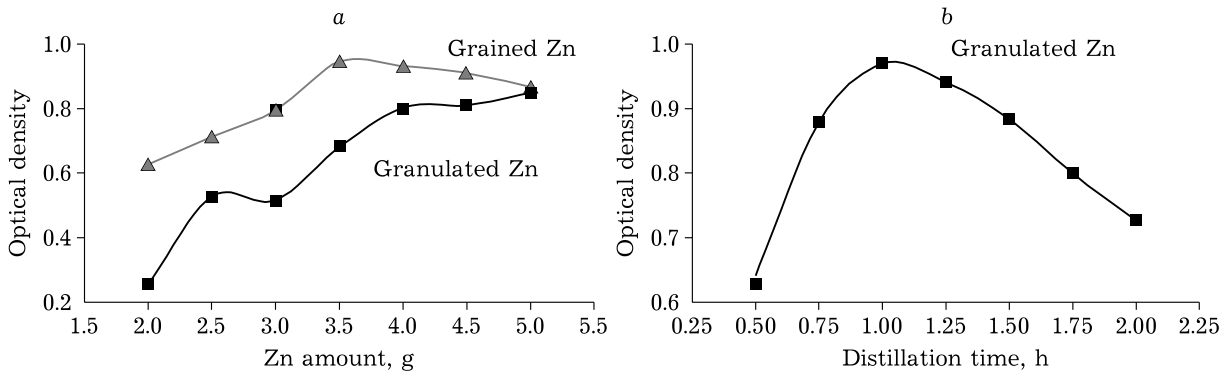

Fig. 1. Dependences of optical density on Zn amount (*a*) and distillation time (*b*).

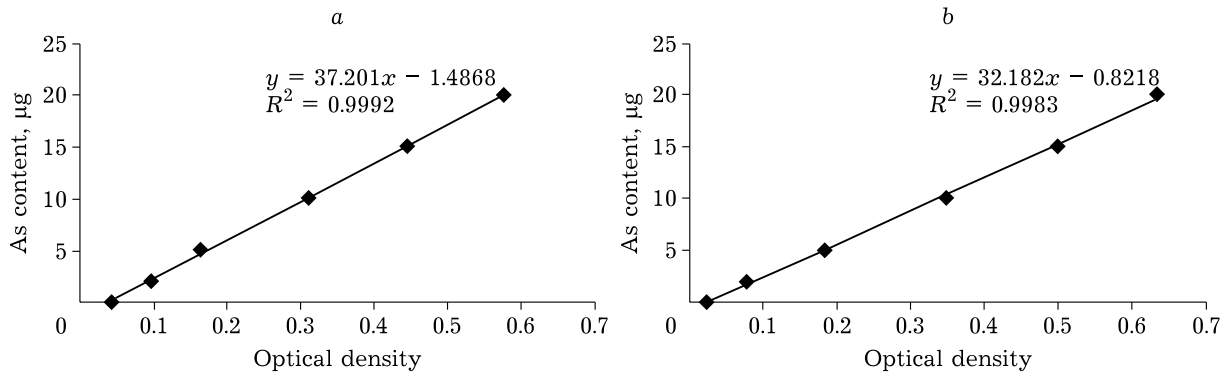

Fig. 2. Calibration curves for the photometric determination of As using granulated (*a*) and grained (*b*) Zn.

In the case if grained but not granulated Zn is used, the reaction proceeds much faster, it is completed within 10–15 min. For this reason, distillation was carried out for 10 min for all solutions. Another advantage of the use of grained Zn (in comparison with granulated one) is elimination of the errors connected with the surface area of the contact between phases, which results in the good convergence of results.

Spectrophotometer graduation

Absolute graduation method using the solutions prepared on the basis of $Na_2HAsO_4 \cdot 12H_2O$ or SSS of As(III) ions was used in the work. Linear equations were obtained for the dependence of optical density on As content, with approximation coefficients (R^2) exceeding 0.99 (Fig. 2). The range of concentrations in the distillation flask was (0–0.4 μg)/mL.

Choice of the optimal method of decomposition for rock and soil samples containing organic matter

As mentioned above, most of the known procedures employ the acid decomposition method using nitric and sulphuric acids, however, this method may lead to unsatisfactory results if organic compounds are present in the sample. We tested the most widespread methods of rock decomposition. The object of investigation was SSS of carbonate and silicate loose sediments SGKhM-1, which is a fine sand-clay fraction of eluvial-deluvial sediments containing As approximately in the amount of 40 g/t and organic matter in the amount of 3–5 wt. %, which requires special decomposition conditions. Results of arsenic determination in the SSS SGKhM-1 after its transfer into solution using different decomposition methods are presented in Table 2.

One can see that decomposition with a mixture of acids HNO_3, H_2SO_4 and $HClO_4$ results in the most complete isolation of As from SSS SGKhM-1, which contains organic matter. Deviation from the certified As content in SGKhM-1 is 19 rel. %. This decomposition method, in comparison with the others, leads to smaller losses of arsenic due to evaporation with the products of oxidation of organic compounds that are present in soil or rock samples. The results of our experiments confirm difficulties in As determination in rocks and soils containing organic matter.

Evaluation of the correctness of arsenic determination

The correctness of the procedure was evaluated from the results of the analysis of rock SSS with certified and approximate As content (carbonate-silicate loose sediments SGKhM-3, alkaline agpaitic granite SG-3, gold-containing ore SZR-2, quartz diorite SKD-1, carbonate background silt SGKh-1). Results of their analysis and evaluation of correctness are shown in Table 3.

One can see in these data that the measured As concentrations in the SSS of rocks exhibit in-

TABLE 2

Determination of As in SSS SGKhM-1 after transfer into solution using different decomposition methods

Decomposition method	Measured value, g/t
HNO_3 and H_2SO_4	19.33±1.93
HNO_3, H_2SO_4 and HF	31.27±3.13
HNO_3/HCl (3 : 1) and H_2SO_4	30.55±3.06
HNO_3, H_2SO_4 and $HClO_4$	32.46±3.25
Na_2CO_3 and KNO_3	1.04±0.19
HNO_3, H_2O_2 and H_2SO_4	3.85±0.69

Note. Here and in Table 3: SSS is State Standard Sample.

TABLE 3

Evaluation of the correctness of rock SSS analysis results

SSS	$C_m \pm \mu$, %	X_m, %	$X_{m\,av}$, %	$\lvert\Theta_m\rvert$, %	S_m^2, %^{2}	t
SGKhM-3	$90.00 \cdot 10^{-3}$	$89.24 \cdot 10^{-3}$	$90.40 \cdot 10^{-3}$	$1.16 \cdot 10^{-3}$	$6.43 \cdot 10^{-6}$	0.353
		$94.18 \cdot 10^{-3}$		$3.78 \cdot 10^{-3}$		
		$88.01 \cdot 10^{-3}$		$2.39 \cdot 10^{-3}$		
		$91.75 \cdot 10^{-3}$		$1.35 \cdot 10^{-3}$		
		$88.80 \cdot 10^{-3}$		$1.60 \cdot 10^{-3}$		
SG-3	$4.00 \cdot 10^{-4}$	$4.24 \cdot 10^{-4}$	$4.10 \cdot 10^{-4}$	$0.14 \cdot 10^{-4}$	$5.79 \cdot 10^{-10}$	0.929
		$4.44 \cdot 10^{-4}$		$0.34 \cdot 10^{-4}$		
		$3.86 \cdot 10^{-4}$		$0.24 \cdot 10^{-4}$		
		$4.05 \cdot 10^{-4}$		$0.05 \cdot 10^{-4}$		
		$3.91 \cdot 10^{-4}$		$0.19 \cdot 10^{-4}$		
SZR-2	1.10±0.03	1.09	1.08	0.01	$5.15 \cdot 10^{-3}$	0.623
		1.04		0.04		
		1.13		0.05		
		0.98		0.10		
		1.16		0.08		
SKD-1	$6.00 \cdot 10^{-4}$	$5.78 \cdot 10^{-4}$	$5.92 \cdot 10^{-4}$	$0.14 \cdot 10^{-4}$	$6.21 \cdot 10^{-10}$	0.718
		$5.61 \cdot 10^{-4}$		$0.31 \cdot 10^{-4}$		
		$6.22 \cdot 10^{-4}$		$0.30 \cdot 10^{-4}$		
		$6.12 \cdot 10^{-4}$		$0.20 \cdot 10^{-4}$		
		$5.87 \cdot 10^{-4}$		$0.05 \cdot 10^{-4}$		
SGKh-1	$16.00 \cdot 10^{-3}$	$15.77 \cdot 10^{-3}$	$15.90 \cdot 10^{-3}$	$0.13 \cdot 10^{-3}$	$8.37 \cdot 10^{-8}$	0.773
		$15.49 \cdot 10^{-3}$		$0.41 \cdot 10^{-3}$		
		$16.10 \cdot 10^{-3}$		$0.20 \cdot 10^{-3}$		
		$16.23 \cdot 10^{-3}$		$0.33 \cdot 10^{-3}$		
		$15.93 \cdot 10^{-3}$		$0.03 \cdot 10^{-3}$		

Notes. 1. $C_m \pm \mu$ – certified concentration and error, %; X_m – results of SSS analysis, %; $X_{m\,av}$ – average As concentration in SSS, %; $\lvert Q_m \rvert$ – mathematical expectation of systematic error, %; S_m^2 – dispersion, %^{2}; t – calculated Student criterion. 2. For designations, see Table 2.

significant scattering and agree with the certified values. The obtained calculated values for Student t-criterion do not exceed the tabulated data ($t_{tabl} = 2.78$) for significance level 0.05 and the number of degrees of freedom $f = n - 1 = 4$. Calculation was carried out using the algorithms for evaluation of metrological characteristics from the methodical instructions and guidelines [25, 26].

In addition, for the purpose of evaluating the correctness of results obtained with the parallel samples of rocks, As content was determined by means of photometry and by means of ICP-MS; results are presented in Table 4. The collected rock samples were volcanoclastic greywacke of the Irendyk formation. The samples were collected near the city of Sibay in the Southern Urals. Sample decomposition for the photometric determination of As was carried out using HNO_3 and H_2SO_4.

Analysis of the obtained results shows that the relative error of photometric determination is 3.0–40.7 rel. %. This does not exceed the requirements of OST 41-08-214-04 [27], according to which the permissible relative error within the concentration range 0.5–20.0 g/t should be not more than 69.9 rel. %.

TABLE 4

Determination of As in parallel samples of volcanoclastic greywacke by means of photometry and mass spectrometry with inductively coupled plasma (ICP-MS)

Sample No.	As content, g/t	
	Photometry	ICP-MS
1	0.98±0.18	1.01±0.51
2	2.25±0.41	2.51±1.26
3	7.02±0.70	4.99±2.50
4	11.89±1.19	15.12±7.56
5	12.55±1.26	19.21±9.61

CONCLUSIONS

1. Optimal parameters for the photometric determination of As in rocks and soils are established. The use of grained Zn for As separation from interfering elements allows shortening the time necessary for analysis. In comparison with granulated zinc, the use of grained Zn excludes the errors connected with the effect of the surface area of contact between phases and provides good divergence in the results.

2. Through evaluation of known decomposition methods, the optimal method was determined for As-containing rocks in which the interfering influence is caused by the organic matter. It is demonstrated that in this case, decomposition with a mixture of acids HNO_3, H_2SO_4 and $HClO_4$ leads to the most complete recovery of As.

3. The data obtained in arsenic determination in rocks by means of photometry provide evidence of the correctness and convergence of determination results.

4. Due to definite advantages of the photometric method (high economic efficiency, high accuracy of determination, low detection limit – 0.1 g/t), it is recommended for mass determinations of As content in rocks and soils (for instance, for the purpose of ecological monitoring and control).

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