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Decomposition of rocks using a mixture of sulfate and ammonium bifluoride for elemental analysis. *UDC 553.22+551.2*

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Abstract. A new methodology has been developed for sampling of rocks for elemental analysis by the atomno-emissions (ICP -AES) and mass spectrometry with inductive-tied plasma (ICP-MS). The objects of the study were international standard samples of rock composition GM (granite), JA-2 (andesite), BHVO-1 (basalt) and JR-1 (rhyolite), in which the main elements (Ti, Al, Mn, Ca, Mg, Fe, Na, K, P) were determined in terms of oxides by the ICP -

AES method, and the microelements (Li, Be, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Mo, Cd, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Pb, Th and U) were determined by the ISP-MS method.

Keywords: *rocks, ammonium sulfate, ammonium bifluoride, elemental analysis, plasma spectrometry methods, new sample preparation method.*

When analyzing rocks, sample preparation is of great importance, which ensures the transfer of sample components into solution, followed by the determination of the element content by various instrumental analysis methods (Zhong et al., 2022). It is the stage of chemical sample preparation that determines the correctness of the entire analysis as a whole, and is the most difficult and lengthy, especially for difficult-to-open geological samples. Therefore, it remains relevant to search for alternative procedures for preparing samples for elemental analysis.

Analytical schemes based on the use of fluoride and ammonium bifluoride are considered as recent achievements in sample preparation for elemental and isotopic analyses of geological samples (Zhang et al., 2019; O'Hara et al., 2017; Liu et al., 2023; Ujvari et al., 2021; Medkov et al., 2022). Unlike acid decomposition, the interaction of minerals with these reagents occurs in the salt melt at temperatures of 190-230 ° C and, therefore, is not limited by the boiling point of the solution, resulting in a more complete opening and subsequent extraction of the sample elements into the solution. After fluorination, the samples are dissolved in acids and a solution is obtained for subsequent instrumental analysis. At the same time, for silicate rocks with a high silicon content, the bulk of ammonium hexafluorosilicate passes into solutions along with rock elements, which increases the total amount of dissolved substances and, as noted above, is an interfering factor in the analysis. Therefore, the next stage of sample preparation is the treatment of a fluorinated sample with nitric acid to remove silicon in the form of SiF_4. This operation is carried out in several stages, first concentrated nitric acid is added to the sample and the solution is evaporated dry, then the dry residue is dissolved again in dilute nitric acid. The entire dissolution procedure is quite lengthy and takes at least 7 hours (Whitty-Leveille et al., 2017).

Previously, (Khanchuk et al., 2015) the possibilities of opening some minerals using a mixture of bifluoride and ammonium sulfate by solid-phase interaction at a temperature of 340-360°C were investigated. In this case, the silicon from the sample is removed into combustion in the form of $(NH_4)_2SiF_6$, which reduces the amount of dissolved solids in the final solution and avoids the formation of poorly soluble fluorides.

The present study is devoted to testing a new method of sample preparation using a mixture of bifluoride and ammonium sulfate for the elemental analysis of some standard samples of silicate rocks by plasma spectrometry (ICP -NPP and ICP -MS).

The material for the study was standard rock composition samples with a wide range of SiO_2 content from 49.94% to 75.45% (from basic to acidic rocks) to test the operability of the technique on similar types of samples: US Geological Survey standards GM (granite) and BHVO-1 (basalt), as well as JR-1 standards (rhyolite) and JA-2 (andesite) Geological Survey of Japan. Ammonium sulfate $(NH_4)_2SO_4$, ammonium bifluoride NH_4HF_2 with purity class "OSH" and nitric acid HNO_3 with purity class "sp" were used as rock-decomposing reagents.

Experiment 1: The sample weight indicated in Table. was mixed with 4 g of ammonium bifluoride and 5 g of ammonium sulfate and then ground in an agate mortar. The resulting mixture in open platinum crucibles was placed in a muffle furnace controller and heated to a temperature of 350 ° C at a rate of ~ 3 degrees / min. The exposure time at the set temperature was 2 hours. Next, the product, cooled to room temperature, was leached by gradually pouring 13% nitric acid into the crucible and decanting the clear solution into a 200 ml measuring flask. After the contents of the crucible were completely dissolved, the solution in the measuring flask was brought to the mark with deionized water type I. The experiment was performed with 5 parallel samples for subsequent statistical processing of the analysis results. An idle experiment was conducted in a similar way.

Experiment 2: The sample weight indicated in

Table 1 was mixed with 4 g of ammonium bifluoride and then ground in an agate mortar. The resulting mixture in open platinum crucibles was placed in a muffle furnace controller and heated to a temperature of 230 ° C at a rate of ~ 3 degrees / min. The holding time at the set temperature was 1 h. Then, the resulting product, cooled to room temperature, was heated in platinum crucibles with 30 ml of concentrated nitric acid for 10 minutes, after which the solution was evaporated to wet salts. The resulting salts were leached by gradually pouring 13% nitric acid into the crucible and decanting the clear solution into a 200 ml measuring flask. After the contents of the crucible were completely dissolved, the solution in the measuring flask was brought to the mark with deionized water type I. The experiment was performed with 5 parallel samples of each sample for subsequent statistical processing of the analysis results. An idle experiment was conducted according to a similar scheme.

Table. Sample weights

№	Experiment	Name of the Sample	Suspension, (g)
1	1	GM granite	1.0012
2	1	JR-1 rhyolite	1.0002
3	1	JA-2 andesite	1.0006
4	1	BHVO-1 basalt	1.0012
5	2	GM granite	1.0007
6	2	JR-1 rhyolite	1.0003
7	2	JA-2 andesite	1.0000
8	2	BHVO-1 basalt	1.0004

The resulting solutions were transferred to 50 ml polypropylene tubes. Traces of hydrofluoric acid (HF) were added to the solutions to prevent possible hydrolysis and polymerization of highly charged ions of the elements.

To perform measurements, 2 ml were taken from the initial solutions and 8 ml of 2% nitric acid were added. In the obtained solutions, the determination of the main elements in terms of oxides TiO_2, Al_2O_3, Fe_2O_3, MnO, CaO, MgO, Na_2O, K_2O, and P_2O_5 was performed using inductively coupled plasma atomic emission spectrometry (ICP-NPP) on an iCAP 7600 Duo spectrometer (Thermo Scientific, USA). The concentrations of the main elements of the studied samples were determined using the ICP-NPP method using the following spectral lines: TiO_2 (λ=334.941), Al (λ=308.215 nm), Ca (λ=318.128 nm), Fe (λ=238.204 nm), Mg (λ=279.079 nm), MnO (λ=257.610), K (λ=766.490 nm), Na (λ=589.592 nm), P (λ=214.914). The calibration characteristics for the ICP-NPP definitions were based on solutions prepared by decomposing standard composition samples from the collection of the Institute of Geochemistry. Favorsky SB RAS (Irkutsk) ST-2A (GSO No. 8771-2005), SSL-1 (GSO No. 3191-85), BIL-1 (GSO No. 7126-94), SKD-1 (GSO No. 2740-83), SSv-1 (GSO No. 6104-91) according to the proposed methodology.

For ICP–MS determinations of trace element composition, the sample solutions were additionally diluted 5 times with 2% HNO_3 to reduce the salt background.

The trace element composition of the studied samples was determined using the ICP-MS method on an Agilent 8800 QQQ spectrometer (Agilent Technologies, USA). The following analytical isotopes were selected for elemental determinations: ^{7}Li, ^{9}Be, ^{45}Sc, ^{51}V, ^{52}Cr, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{71}Ga, ^{75}As, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{95}Mo, ^{111}Cd, ^{118}Sn, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{178}Hf, ^{181}Ta, ^{183}W, ^{208}Pb, ^{232}Th и ^{238}U. The set of elements was determined by the instrumental capabilities of the ICP-MS method, the specifics of the sample preparation technique, as well as the geochemical significance of some elements, in particular REE and Nb/Ta, Zr/Hf pairs, given the fact that these elements are concentrated in hard-to-open accessory minerals. Thus, the accuracy of determining the elements may indicate in a certain way the applicability of the described technique for the analysis of silicate rocks.

To suppress spectral polyatomic interferences in the mass range from 45 to 157, in which the most intense overlaps are usually observed, the instrument was used in the background correction mode using a helium-filled octopole collision cell with energy discrimination (ORC technology). There were no significant overlaps from double-charged ions of the $^{90}Zr^{++}$ type on $^{45}Sc^{+}$, or isobaric interferences that could not be eliminated using ORC technology.

A series of calibration solutions for ICP-MS analysis was prepared from multi-element standard solutions of the detected ions. We used Multi-element Calibration Standard 1 (No. 8500-6944): Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th, Tm, Y, Yb; Multi-element Calibration Standard 2A (No. 8500-6940): As, Ba, Be, Cd, Co, Cr, Cs, Cu, Ga, Li, Ni, Pb, Rb, Sr, U, V, Zn; Multi-element Calibration Standard 3 (No. 8500-6948): Hf, Sn and Multi-element Calibration Standard 4 (No. 8500-6942): Mo, Nb, Ta, W, Zr (Agilent Technologies, USA) by weight method. The concentrations of the components to be determined in the calibration solutions ranged from 0.01 to 1000 micrograms/dm^3.

The internal standard in the ICP-MS analysis was 115In, which was injected into the sample supply system online at a concentration of 20 micrograms/ dm3.

As a result, the conditions of the ICP analysis included: the purity of the reagents in accordance with the requirements for ICP-MS and ICP-NPP analysis, significant dilution of the studied solutions to reduce the salt background, rational choice of analytical isotopes, and the use of certified solutions for calibration of the device. All this made it possible to minimize the errors in the results of determining the elements.

Instrumental determinations of chemical element concentrations were performed at the Primorsky Center for Local, Elemental and Isotope Analysis of the Far Eastern Geological Institute of the Far Eastern Branch of the Russian Academy of Sciences.

During sample preparation of standard rock samples according to the methods given in the experimental part, their complete dissolution occurs. As mentioned above, when using ammonium bifluoride for sample preparation to remove silicon in the form of SiF4 and transfer the fluorinated sample to a solution, the sample must be dissolved in concentrated nitric acid, followed by evaporation of the resulting solution to wet salts (dry) at a temperature of 160 °C (Zhang et al., 2019). Next, to determine the content of the elements, it is necessary to dissolve the evaporated sample in nitric acid again. When using a mixture of NH_4HF_2 and $(NH_4)_2SO_4$ for sample preparation, rock samples are immediately completely dissolved in a dilute nitric acid solution without pretreatment with concentrated.

For the complete decomposition of minerals, the interaction of rocks with a mixture of bifluoride and ammonium sulfate was used when heated to 350 ° C for 2 hours. It was found that after such a procedure, all components of the studied samples completely dissolve in 13% nitric acid. The elemental analysis of the micro- and macro components of the solutions showed a good match with the certified characteristics, which indicates the completeness of the transition of the rock components into the solution. The mechanism of interaction of minerals that make up rocks with bifluoride and ammonium sulfate is investigated. It has been established that combining the stages of fluorination and sulfatization makes it possible to effectively open silicate rocks. This is due to the breaking of Si-O bonds with the participation of NH_4HF_2 to form simple and complex fluorides and the conversion of insoluble fluorides of the elements of the analyzed samples into more soluble sulfates with the participation of $(NH_4)_2SO_4$. It is shown that silicon is removed in the form of $(NH_4)_2SiF_6$ during sample preparation, resulting in a significant reduction in the mass of dissolved salts, since silicon is the main component of silicate rocks. The advantage of the proposed technique, for example, in comparison with acid decomposition is its expressiveness and completeness of opening by reducing the number of stages in the process of decomposition of rocks.

Thus, the research carried out made it possible to develop a new method of sample preparation of silicate rocks for subsequent multi–element analysis using modern instrumental methods - ICP-NPP and ICP-MS. The decomposition of rocks was studied using a mixture of sulfate and ammonium bifluoride for subsequent elemental analysis. It has been established that the combination of fluorination and sulfatization processes makes it possible to effectively open rocks due to the breaking of Si-O bonds with the participation of NH_4HF_2 and the transfer of insoluble fluorides of raw material elements into more soluble sulfates with the participation of $(NH_4)_2SO_4$.

It has been shown that when using a mixture of NH_4HF_2 and $(NH_4)_2SO_4$, it is possible to more fully open mineral raw materials compared with using only ammonium bifluoride. In this case, the silicate matrix is discharged into the gas phase in the form of $(NH_4)_2SiF_6$, which, in turn, reduces the mass of dissolved substances in the final analyzed solution. A mixture of NH_4HF_2 with $(NH_4)_2SO_4$ can be recommended as a promising new reagent for the decomposition of silicate rocks during sample preparation for subsequent elemental analysis using modern instrumental methods.

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