

IMPROVEMENT OF TREATMENT METHODS IN ANALYSIS OF CARBON MOUNTAIN BREEDS BY ICP-MS

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Abstract- An algorithm was developed for chemical sample preparation of carbonaceous rocks for the subsequent ICP-MS analysis of impurity elements. The impact is assessed and the optimal conditions for the preliminary heat treatment of carbonaceous rocks are selected. The possibility of intensification of the preliminary heat treatment stage with the help of oxidizing additives is shown.

Keywords: Carbonaceous Rocks, Mass Spectrometer with Inductively Coupled Plasma, Sample Preparation, Rare Earth Elements.

1. INTRODUCTION

Physical and physico-chemical methods for the study of substances are widely included in the practice of studying rocks. Currently, such methods as emission spectral and laser, neutron activation and atomic adsorption, mass spectrometry with inductively coupled plasma, etc., are increasingly being used. Their advantages are high performance and sensitivity, the ability to determine a wide range of elements and good reproducibility [1] disposal of radioactive waste. Each of these methods has its advantages and disadvantages. However, for the analysis of geological objects, they are not always optimal, since they do not combine the sensitivity, accuracy, multi-elementally and performance of the analysis. The emergence of the method of mass spectrometry with inductively coupled plasma (ICP-MS) made it possible to determine the elements with extremely low concentrations against the background of the matrix (the concentration range of the determined elements is 9 orders of magnitude) [2, 3]. However, to conduct a reliable ICP-MS analysis of geological samples, there is a need for a preliminary analysis of the object for its matrix component.

The spectrum of geological samples is very wide. Recently, special attention has been given to metamorphic rocks, in particular, sedimentary-metamorphic strata of black shale type, as unusual geological and geochemical objects. They fix the turning

points in the history of the stratosphere, are the most important source formations, are characterized by powerful geochemical anomalies and are often ore-bearing [4]. A feature of this type of rocks is the association of metals with dark schistose sedimentary rocks enriched in carbonaceous matter. Such rocks often contain significant amounts of heavy metals, especially copper, nickel, cobalt, vanadium, molybdenum, uranium, gold, zinc, lead, as well as the rare metal component, forming rich complex ores of industrial interest [5].

Great interest are finds in carbonaceous rocks of rare-earth elements (REE), among which the main role is played by phosphate La, Nd and Ce (monazite-florentsit). Less common are aluminosilicate phosphate Y, Gd, and La and Ce oxide [6].

A distinctive feature of sedimentary and metamorphic rocks is that they contain scattered and concentrated forms of organic substances (OS). Under the generalized term OV is meant carbon compounds with hydrogen, hetero-elements (O, N, S) and a certain amount of impurity elements (Si, P, O, metals). In general, OM is a complex mixture of various compounds [7].

The analysis of this kind of materials is of particular interest and complexity for chemical and analytical work. In addition to the difficulty of opening the matrix of rocks as such (due to the content of a wide variety of components and accessory minerals, which, in turn, are not easily decomposed), the content of carbonaceous matter in the rocks prevents the complete transfer of the sample into the solution due to inertness to the used acids (limited by the features of the equipment used). Thus, a detailed study of the composition of carbonaceous rocks is an urgent task at present.

2. ANALYZED ELEMENTS

For geological and geochemical studies, the main (rock-forming) elements, admixture elements and trace elements are identified. The main (rock-forming) elements are dominant in almost all geological objects: Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P. The total content of rock-forming elements is close to 100%.

Elements-impurities include elements that are present in an amount of 1-0.1%. The content of trace elements in the rock is below 0.1% [8, 9].

Elements-impurities can include almost all elements of the periodic table depending on the type of rock. As a criterion for the selection of impurity element groups, one can take the physical properties of the elements (ionic radius, charge, etc.). For geochemical studies, the most convenient classification of impurity elements is according to the proximity of ionic radii and charges, since such groups of elements, as a rule, exhibit the same behavior in geochemical processes.

The main groups of elements [8] are presented in Figure 1. Three groups of impurity elements can be distinguished - large ion lithophyls (LIL - large ion lithophyls), highly charged elements (HFS - high field strength elements) and transition (transit) elements. According to the diagram, large-ion lithophilam (LIL) includes Cs, Rb, K, Ba. Sometimes this group of elements includes Sr, divalent Eu, Pb. These elements are characterized by a large ionic radius and low charge (valence 1, less often 2) and the greatest mobility in various geological processes.

The group of high-charge elements (HFS) includes such elements as Sc, Y, Th, U, Pb, Zr, Hf, Ti, Nb, Ta, as well as the group of rare earth elements (REE, REE (rare earth elements): La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu. Sometimes this group includes yttrium, the atomic radius of which is close to REE [10]. Highly charged elements are the least mobile with various superimposed processes, in connection with which they are sensitive indicators of geochemical processes. The most attention among the elements of impurities is paid to REE. REEs have similar chemical properties, ionic radii, and are stable in the trivalent state.

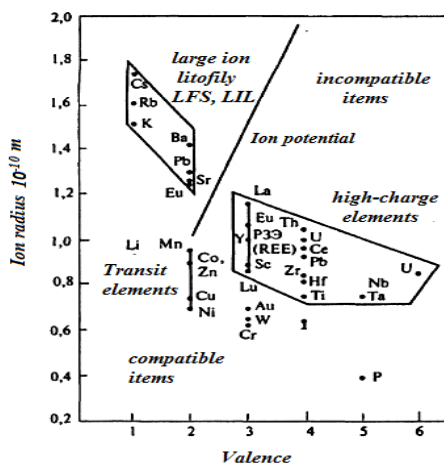


Figure 1. Diagram for the elements of impurities: the ionic potential (charge-to-radius ratio), equal to 2, separates the fields of large-ion lithophyls and high-charge elements [8]

Some differences in chemical behavior are determined by a slight but constant increase in the ionic radius with an increase in the atomic number. These differences are used in the simulation of various geological processes. REE have a number of features, among which the

prevalence in nature can be distinguished. Elements with even numbers are more stable than odd, therefore they are found in natural objects in higher concentrations. As a result, the distribution curve of elements has a zigzag appearance (Figure 2). Therefore, when constructing graphs of the distribution of REE use the procedure of normalization to the standard. This procedure is used very widely in interpretation of geochemical data [8, 10, 12].

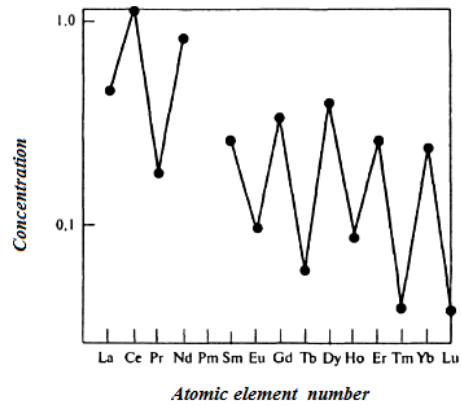


Figure 2. Chart of concentration of rare-earth element (logarithmic scale) - atomic number [8]

REE are one of the least mobile elements, which are weakly influenced by the processes of hydrothermal change and low-temperature metamorphism, therefore their content most correctly reflects the composition of primary igneous or sedimentary rocks and the degree of melting of the mantle substance. The distribution of REE does not undergo significant changes in the processes of sedimentation, lithogenesis and metamorphism. Sedimentary strata, even under conditions of high pressures and temperatures, inherit geochemical features characteristic of the original rocks [8, 11, 13].

In general, most often for geochemical interpretation, the following impurity elements are required: Be, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Pb, Th, U [11, 13].

Analysis of the rock-forming elements (Al, Ti, Ca, Mg, Mn, Fe, Si) gives information about the typification and the nature of the genesis of the rock. The definition of rock-forming elements is an integral part of geochemical research.

The combination of data on the content of basic elements and impurities gives a complete geochemical picture. That is why a reliable determination of the elemental composition of geological samples is crucial for a whole complex of geochemical studies.

3. EXPERIMENTAL PART

3.1. Instruments and Equipment

Investigation were performed on an Agilent 7700 mass spectrometer with inductively coupled plasma (Agilent Technologies, USA). The microwave system Milestone Start D (Italy) for acid decomposition used. LOIP LF-7/11-G1 muffle furnace was used for pre-baking.

The mass spectrometer with inductively coupled plasma can be considered a combination of a conventional mass spectrometer with a plasma source of excited particles. The sample entry system includes a peristaltic pump, sprayer, spray chamber. The test solution is sucked in by a peristaltic pump at a rate of 0.1 ml per minute. An aerosol is produced from the sample solution, passing through a two-pass spray chamber (Figure 3).

The fine aerosol obtained from the sample (coming out of the spray booth) directly enters the tube that feeds into the horizontally mounted plasma torch. The gas entering the three-cylinder plasma torch is called plasma-forming, auxiliary gas and carrier gas (supplied to the nebulizer). A four-turn coil (inductor) is worn, to which a high-frequency signal is supplied (27.12 MHz) at the end of the burner. Collisions of argon atoms are ensured in a strong high-frequency field (i.e., plasma "burning" is maintained) after the plasma is enriched with electrons. The temperature is reached in the range from 8,000 to 10,000 degrees Kelvin at the center of the plasma. The sample turned into an aerosol instantly disposes of the solvent and ionizes [14].

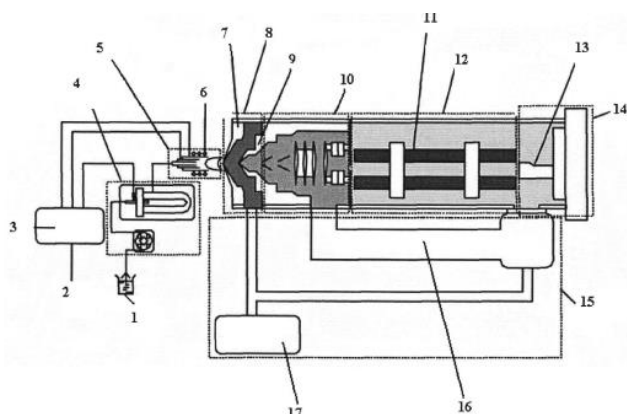


Figure 3. Diagram of mass spectrometer with inductively coupled plasma by Agilent 7700: 1- sample; 2- argon feed; 3- gas flow regulator; 4- sample input system; 5- inductively coupled plasma; 6- high-frequency generator; 7- selecting a cone; 8- interface; 9- separating cone; 10- a system of lenses focusing the flow of ions; 11- quadrupole mass filter; 12- analyzer; 13- electron multiplier; 14- the registrar; 15- vacuum system; 16- turbomolecular pump; 17- rotary pump.

Then the ions enter the quadrupole analyzer, which consists of 4 metal rods with a hyperbolic cross section. The rods are placed parallel to each other; they are connected to high-frequency and constant voltage. The rods act as a filter for the masses by changing these stresses. Only ions with a specific mass-to-charge ratio (m/z) are able to pass through the center of the quadrupole with a specific combination of applied voltages. The ions are recorded by the electron multiplier after passing through the quadrupole.

The output is a mass spectrum that displays the dependence of the analytical signal on the ratio of mass to charge (Figure 4).

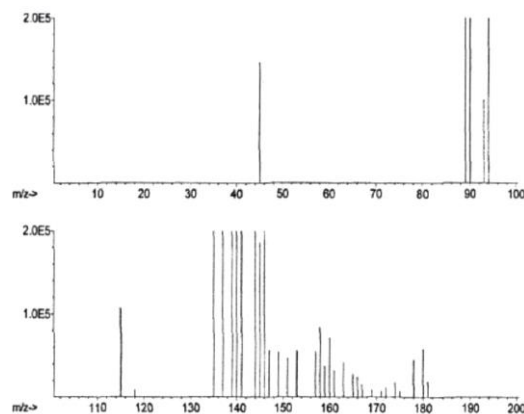


Figure 4. Mass spectrum of REE

3.2. Search for Effective Ways to Open Carbonaceous Rocks

Using the method of ICP-MS allows you to work with weights samples in a few milligrams. The choice of a representative sample depends on the distribution of the analyzed elements. According to the literature data [15], a weight of 0.05-0.1 g is representative for the determination of REE and most of the impurity elements. Used standard samples meet international requirements for homogenization.

Currently, there are many schemes for acid decomposition of geological matrices [15, 16]. The acid decomposition method for rocks, summarized from literature data, was chosen as the reference scheme for chemical sample preparation.

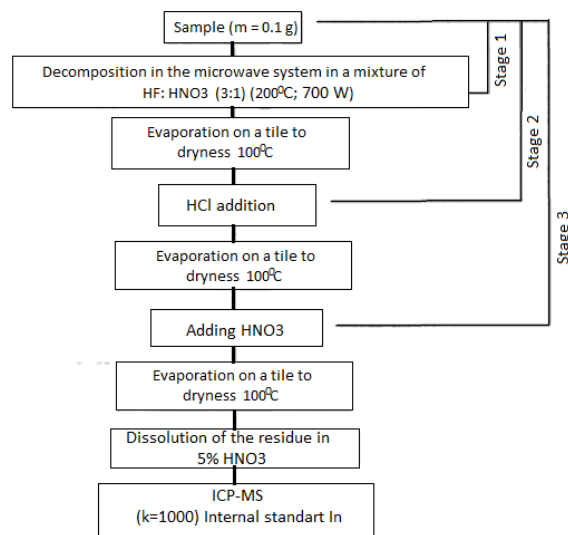


Figure 5. Sample preparation scheme No. 1

A sample weighing 0.1 g was processed with a mixture of HF: HNO₃ (3:1) and subjected to microwave exposure in a closed system at a temperature of 200 °C and power of 700 W (stage 1) (Figure 5). After that, the sample was evaporated to dryness, treated with concentrated HCl (stage 2). The resulting chloride solution was again evaporated, and the precipitate was transferred to a nitrate medium by dissolving in

concentrated nitric acid (stage 3). The results of ICP-MS analysis of the obtained solutions are given in Table 1 ($n=5, P=0.95$). The analysis of the obtained data showed that the complete transfer of studied samples into solution does not occur. At same time, significant underestimation of results is observed for heavy REE and Y.

Table 1. The results of ICP-MS analysis of the obtained solutions

Elements	SCo-1		SBK-1	
	C_{attest}	C_{ICP-MS}	C_{attest}	C_{ICP-MS}
Be	2,4*	2,1±0,2	2,0±0,4	2,2±0,2
Sc	20±3	18±2	23±4	12,2±1,3
V	122±15	113±14	148±18	154±17
Cr	116±8	129±16	128±10	165±18
Co	20±3	19±2	13±2	11,9±1,3
Ni	50±7	56±7	39±6	42±5
Cu	39±7	35±4	34±6	31±3
Zn	97±13	83±10	96±11	84±9
Ga	18±3	17±3	21±2	20±3
Rb	112±11	102±12	140±10	140±15
Sr	142±15	136±16	150±15	144±16
Y	26±4	8,7±1,1	28±5	12,9±1,4
Zr	176±16	159±19	176±16	164±18
Nb	12±2	10,7±1,3	11±2	12,5±1,4
Cs	4,0±0,7	4,0±0,5	4,4±0,8	4,6±0,5
Ba	376±46	348±42	720±120	460±51
La	28±5	26±3	30±5	26±3
Ce	53±8	55±7	58±11	61±7
Pr	6,2±1,2	6,9±0,8	6,5*	6,5±0,7
Nd	25±4	26±3	28±5	25±3
Sm	5,4±0,8	4,8±0,6	5,7±0,9	4,9±0,5

The sample preparation scheme No. 1 used was upgraded by adding a 4-hour stage of holding the sample in an open system with the gradual addition of 10 ml of HF at 70 °C to maximize the removal of silicon in the form of fluoride, thereby avoiding the formation of further complex aluminosilicate. The scheme of chemical sample preparation can be described as follows. A sample weighing 0.05 g was treated with 10 ml of concentrated HF for 4 hours at a temperature of 70 °C for maximum distilling of silicon as fluoride. Then, 1 ml of concentrated HNO₃ was added to the reaction mixture and decomposition was performed in a microwave oven at a furnace power of 1000 W with a gradual increase in temperature to 220 °C. The samples were quantitatively transferred to 50 ml Teflon cups, evaporated "before the drop" after cooling.

The residue was treated with 1 ml HClO₄ and left overnight. After that, the sample was evaporated to dryness. Metal fluorides were destroyed by double evaporation of a dry residue of a sample of 6.2 M HCl at a temperature of 90 °C [16]. Chlorides were converted to nitrates by the addition of concentrated HNO₃ twice. Finally, the dry residue was dissolved in a 15% solution of HNO₃ (Figure 6). The scheme of sample preparation is shown in Figure 6. Comparison of the results of the two sample preparation schemes are shown in Table 2.

Experiment to determine the optimal weight of the sample showed that a mass of 0.05 g is sufficient for a reliable determination of the elements being analyzed (Table 2).

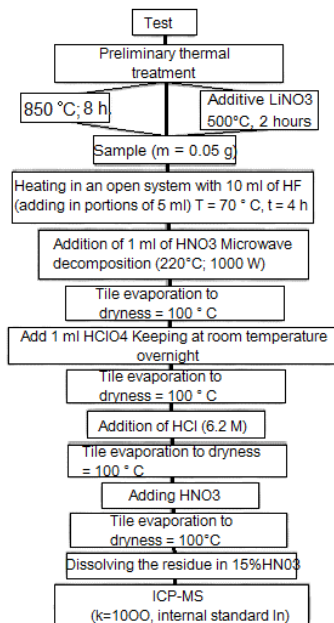


Figure 6. Sample preparation scheme No. 2

Table 2. Comparison of ICP-MS results of determination of impurity elements in SCo-1 ($n=7, P=0.95$) according to two sample preparation schemes, g/t

Element	C_{attest}	C_{ICP-MS} (scheme №1)	C_{ICP-MS} (scheme № 2)
Be	2,4*	2,1±0,2	2,2±0,2
Sc	20±3	18±2	19±2
V	122±15	113±14	113±14
Cr	116±8	129±16	130±16
Co	20±3	19±2	20±2
Ni	50±7	56±7	53±7
Cu	39±7	35±4	35±4
Zn	97±13	83±10	89 ±11
Ga	18±3	18±3	18±3
Rb	112±11	102±12	109±13
Sr	142±15	136±16	135±16
Y	26±4	8,7±1,1	12,1±1,5
Zr	176±16	159±19	166±20
Nb	12±2	10,7±1,3	10,8±1,3
Cs	4,0±0,7	4,0±0,5	4,0±0,5
Ba	376±46	348±42	351±42
La	28±5	26±3	25±3
Ce	53±8	55±7	53±6
Pr	6,2±1,2	6,9±0,8	7,3±0,9
Nd	25±4	26±3	25±3
Sm	5,4±0,8	4,8±0,6	4,9±0,6
Eu	1,2±0,2	1,08±0,13	1,03±0,12
Tb	0,74*	0,42±0,05	0,49±0,06
Gd	4,5±0,8	3,29±0,05	3,6±0,4
Dy	4,4*	1,9±0,2	2,4±0,3
Ho	0,92*	0,40±0,05	0,48±0,06
Er	2,4*	1,07±0,05	1,38±0,17
Tm	0,33*	0,19±0,02	0,24±0,03
Yb	2,7±0,4	1,4±0,2	1,6±0,2
Lu	0,40±0,07	0,24±0,03	0,27±0,03
Hf	4,7±0,7	4,2±0,5	4,3±0,5
Ta	0,7*	0,76±0,09	0,77±0,09
W	3,3*	3,1±0,4	3,0±0,4
Pb	14,9±2,8	17±2	17±2
Th	7,1±1,1	7,5±0,9	7,3±0,9
U	1,65±0,23	1,6±0,2	1,60±0,2

Permanent-magnet synchronous motors are used in a wide range of electromechanical systems because they are simple and can be easily controlled. The steady-state torque-speed characteristics fulfil the controllability criteria over an entire envelope of operation. In this paper a bounded controller is designed and sufficient criteria for stability are satisfied. Different reference velocity, loads, and initial conditions are studied to analyze the tracking performance of the resulting system.

4. CONCLUSIONS

Thus, an algorithm was developed for the chemical sample preparation of carbonaceous rocks for the subsequent ICP-MS analysis of impurity elements. The impact is assessed and the optimal conditions for the preliminary heat treatment of carbonaceous rocks are selected. The possibility of intensification of the preliminary heat treatment stage with the help of oxidizing additives is shown.

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BIOGRAPHIES



Tarana Kamil Nurubeyli was born in Azerbaijan on February 17, 1979. She graduated as Master degree in Honors from Baku State University, Baku, Azerbaijan in 2001. Since 2004 she was as Research Assistant of Institute of Physics, Azerbaijan National Academy of Sciences, Baku, Azerbaijan. Since 2011 she received Candidate of Physics-Mathematical Sciences degree (Ph.D.). Her scientific interests are design of mass analyzers, estimation of assembly and designing of time of flight energy-mass analyzers, carrying out of tests of developed devices, planning and carrying out of scientific researches with a chromatograph mass spectrometer. She is the member of Russian Mass-Spectrometry Society.



Arif Mamed Hashimov was born in Shahbuz, Nakhchivan, Azerbaijan on September 28, 1949. He is a Professor of Power Engineering (1993); Chief Editor of Scientific Journal of "Power Engineering Problems" from 2000; Director of Institute of Physics of Azerbaijan National Academy of Sciences (Baku, Azerbaijan) from 2002 up to 2009; and Academician and the First Vice-President of Azerbaijan National Academy of Sciences from 2007 up to 2013. He is laureate of Azerbaijan State Prize (1978); Honored Scientist of Azerbaijan (2005); Cochairman of International Conferences on "Technical and Physical Problems of Power Engineering" (ICTPE) and Editor in Chief of International Journal on "Technical and Physical Problems of Engineering" (IJTPE). Now he is a High Consultant in "Azerenerji" JSC, Baku, Azerbaijan. His research areas are theory of non-linear electrical Networks with distributed parameters, neutral earthing and ferroresonant processes, alternative energy sources, high voltage physics and techniques, electrical physics. His publications are 350 articles and patents and 5 monographs.



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Kamil Zulfuqar Nuriyev was born in 1939 in Baku, in 1956. He graduated from Azerbaijan State University, Baku, Azerbaijan. He begun the scientific activities at Institute of Physics, Azerbaijan National Academy of Sciences, Baku, Azerbaijan, and defended his thesis in 1973. He was engaged in development mass spectrometers in Institute of Space Research of Natural Resources, Baku, Azerbaijan since 1976 and continued his activity in the IPh until 2007. The subject of his research activities is the development and application of mass spectrometry instruments. During this time, he engaged in improving the technical parameters as serial devices as laboratory models of its own design.



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Sabina Ilham Hasanova was born in Baku, Azerbaijan, on January 01, 1972. She received the M.Sc. degree in Power Engineering from Azerbaijan State Oil Academy (Baku, Azerbaijan) in 1996. Since 2005 she is a candidate of technical sciences (Ph.D.) and engaged in development and further improvement of analytical abilities of Mass-spectrometer. She has over 20 publications in Azerbaijan and abroad, also is author and coauthor of several inventions. She has also participated in several international conferences.