ICP-AES ANALYSIS OF SILICATE MATERIALS

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For routine multielement analysis of silicate materials the instrumental methods for determination are widely useful, mainly, X-ray diffraction (XRD) and inductively coupled plasma atomic emission spectrometry (ICP-AES). XRD provides high accuracy due to homogenization of investigated material by fusion and using reference materials with matrix composition comparable to sample analyzed. For ICP-AES determination preliminary sample dissolution is required however effect of matrix composition is lower than for XRD method, determination of elements is independent and sample amounts are considerably smaller.

Limiting stage of ICP-AES determination is sample preparation. It should provide express and total dissolution of material and exclude silicon losses as SiF_4. On this reason sample decomposition in closed vessels heated by microwaves (MW) is promising. The most attention in the paper is paid to reaction mixture composition.

Dissolution was carried out in the microwave system MARS5 (CEM Corp., USA). Vessels from polymer materials were used (volume 100 ml, max working temperature - 300°C, pressure - 100 atm.) under simultaneous temperature and pressure monitoring. Determination of elements was carried out using ICP-AES spectrometer IRIS Intrepid II XDL duo (Thermo Electron Corp., USA).

For sample decomposition of silicates the most effective reagent preventing volatilization of silicon tetrafluoride - hydrofluoroboric acid - was used which was formed directly in the reaction vessel. During experiments sample mass and boric acid, volumes of HCl and HF, number of decomposition steps, temperature and time of microwave influence has been varied. MW power was changed depending on number of simultaneously decomposed samples and total acid volume in all vessels (300 for 1-2, 600 – for 3-5 and 1200 W - for 6 and more). It was shown that chosen conditions of MW sample preparation provide complete dissolution of silicate materials and are applicable for following ICP-AES determination.

Decomposition of samples. Samples (0.05 g) were placed into the vessels and mixed with boric acid (2 g), then, conc. HCl (5 ml) and HF (5 ml) were added. The vessels were closed and placed into the microwave oven. Heating at 200°C, 10 min ramping and 20 min holding at temperature were specified. The vessels were air cooled after decomposition, opened, the solution were transferred into flasks and diluted to 50 ml with distilled water.

For *ICP-AES determination* aliquots of solutions were diluted with distilled water and analyzed using internal standard which was added into both sample and reference solutions. Cadmium was chosen as internal standard because of does not create line interferences, undergo to spectral and matrix influences with analyzed elements and has analytical lines on a both slits. For calibration the solutions prepared from standard reference materials (SRMs) of silicate rock materials were used. Analytical lines used for ICP-AES determination are presented in the tab. 1.

Table 1

Analytical lines used for ICP-AES determination

Element	Line	Element	Line	Element	Line
Al	396.152(85)* 308.215(109)	Mg	285.213(118) 280.271(120)	Mn	257.610(130) 259.373(129)
Ca	317.933(105) 315.887(106)	P	214.914(156)	Na	818.326(41) 588.9995(41)
Fe	259.837(129) 239.562(140)	Si	212.412(158) 251.612(133)	Cd (internal standard)	214.438(157) (1 slit)
K	766.491(44)	Ti	323.452(104) 334.941(100)		228.802(146) (2 slit)

* In brackets the order of a spectrum is given

To obtain maximum analytical signal, the conditions of ICP-AES measurement were optimized by gas flow rates. The following optimum conditions were found for axial view: integration time - 10 s,

nebulizer gas flow rate - 0.5 l/min, auxiliary gas flow rate - 0.7 l/min, sample gas flow rate - 1.85 ml/min.

Results (tab. 2) obtained using technique proposed 6are in a good agreement with certified concentrations of rock-forming elements in SRMs. Especially a high correlation of silicon determination results which did not reached in a previous papers [2-4] should be noted. Total time consumption (versus classical fusion technique) is reduced in several times, particularly; decomposition time was decreased to 1 hour for 12 simultaneously prepared samples. Decomposition and analysis of 12 samples can be performed during 1 day's work. The suggested methodology can be used as a comparative approach for analysis of silicates and if amount of material is limited.

Table 2

Determination results of macro-components in different standard reference materials of silicate rock samples (KPT-1 − quartz diorite, MGT-1 − granite, OPY-1 − ultramafic rock, 55a − chamotte, SGD-1A – gabbro, SNS-1A − nepheline syenite)

Sample		SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	K_2O	Na_2O	MnO	TiO_2	P_2O_5	loi
KPT-1	Certified	54.14	14.41	6.89	4.30	12.24	1.65	2.61	0.14	0.90	0.17	1.89
	Found	53.90	13.70	7.06	4.60	12.28	1.56	2.97	0.14	0.90	0.32	
MGT-1	Certified	72.35	14.04	1.15	0.38	2.42	4.67	3.65	0.06	0.29	0.13	0.07
	Found	71.91	13.94	1.22	0.42	2.48	4.49	3.59	0.06	0.29		
OPY-1	Certified	44.05	7.95	7.80	21.43	11.84	0.04	1.11	0.18	0.38	0.03	4.65
	Found	44.78	7.65	8.28	23.83	12.21	0.16	2.08	0.18	0.40	0.04	
55a	Certified	58.57	34.0	0.47	0.84	1.79	2.50		0.02	1.24		
	Found	59.40	33.52	0.47	0.85	1.67	2.46	1.08	0.02	1.09		
SGD-1A	Certified	46.39	14.84	11.04	7.03	11.54	2.96	2.82	0.17	1.71	1.00	
	Found	47.07	14.81	11.39	7.41	12.04	2.83	3.34	0.17	1.73	1.5	
SNS-1A	Certified	40.18	28.25	7.13	1.01	3.25	(3.3)	12.20	(0.04)	0.24	0.51	3.50
	Found	40.13 ±0.06	28.28 ±0.044	7.12 ±0.012	1.01 ±0.001	3.24 ±0.006	3.28 ±0.03	11.97± 0.0005	0.04	0.24	0.60	
	RSD	0.004	0.005	0.011	0.010	0.016	0.01	0.001				

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