ICP-AES Silicate Analysis of Geological and Technical Materials with Concentration Ratio Calibration

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Abstract. In solving the problem of improving the accuracy of the ICP-AES procedures for silicate analysis of geological and technical materials, an approach based on an optimal combination of directional sample preparation methods with concentration ratio calibration was proposed and implemented. The known methods of sample preparation have been modernized and new ones have been developed with improved efficiency and cost-effectiveness in comparison with existing procedures: acid dissolution of samples in closed teflon tubes-autoclaves under heating (geological materials with silicate, carbonate matrices, iron ore raw materials) and alkaline fusion with lithium hydroxide in silver crucibles (ilmenite, zirconium concentrates, refractories). The equations for the calibration dependences, which provide the best metrological characteristics of ICP-AES silicate analysis procedures compared with other calibration options were obtained. The algorithm of ICP-AES measurements, as well as comparative characteristics of the developed procedures were given.

Keywords: geological and technical materials, silicate analysis, ICP-AES, concentration ratios calibration.

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АЭС-ИСП силикатный анализ геологических и технических материалов с градуировкой по отношениям концентраций

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Аннотация. В решении проблемы повышения точности методик АЭС-ИСП силикатного анализа геологических и технических материалов предложен и реализован подход, основанный на оптимальном сочетании направленных способов пробоподготовки и градуировки по отношениям концентраций. Модернизированы известные и разработаны новые способы пробоподготовки с улучшенными показателями эффективности и экономичности в сравнении с существующими процедурами: кислотное растворение проб в закрытых тефлоновых пробирках – автоклавах при нагревании (геологические материалы с силикатной, карбонатной матрицами, железорудное сырье) и щелочное сплавление с гидроксидом лития в серебряных тиглях (ильменитовые, цирконовые концентраты, огнеупоры). Получены уравнения для градуировочных зависимостей, обеспечивающие лучшие метрологические характеристики АЭС-ИСП методик силикатного анализа по сравнению с другими вариантами градуировки. Приводятся алгоритм АЭС-ИСП измерений, а также сравнительные характеристики разработанных методик.

Ключевые слова: геологические и технические материалы, силикатный анализ, АЭС-ИСП, градуировка по отношениям концентраций.

Introduction

It is incalculable the importance of chemical analysis of geological and technical materials. Among the variety of solved problems, silicate analysis historically occupies a special place – the determination of the mass contents of rock-forming oxides SiO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O, K_2O, the sum of which can reach 99 % of the mass of rocks. Due to the very high requirements for measurement accuracy at the level of 0.05–0.5 % rel., classical chemical methods occupy a large share in silicate analysis [1, 2]. However, despite ensuring the required measurement accuracy, these methods have a number of disadvantages: they are single-element, time-consuming, require a large consumption of toxic reagents in some cases, and are often associated with a subjective assessment of the completion of the relevant procedures. Therefore, one of the main trends of modern silicate analysis is the involvement of alternative instrumental methods, in particular, atomic emission spectrometry with inductively coupled plasma [3, 4]. The certified ICP-AES procedures allow determining the mass

fractions of rock-forming elements oxides simultaneously, however, measurement errors exceed those for classical analogues [5–7]. To improve the accuracy of ICP-AES measurements in our works [8–11], a method with concentration ratio calibration has been implemented, which previously successfully was used in the ferrous and non-ferrous metals analysis [12, 13].

This article presents the algorithm of ICP-AES measurements, as well as comparative characteristics of the developed procedures.

Materials and methods

ICP-AES measurements were carried out on iCAP 7400 Duo and iCAP PRO XP Duo series spectrometers (Thermo Fisher Scientific, USA) with simultaneous recording of the intensities of elements analytical lines and double observation of plasma in the wavelength range from 166 to 847 nm. The spectrometers are equipped with iTEVA and/or Qtegra software, each of which allows calibration of the spectrometer by concentration ratios. Sample preparation was carried out using resistive heating systems HotBlock 200 (Environmental Express, USA) and HOTBOX 300 (Siberian Analytical Systems LLC, Krasnoyarsk). The rock samples, ores, concentrates, standard reference materials were objects of analysis. A detailed description of the relevant ICP-AES measurement procedures is given in [8–11].

Results and their discussion

The ICP-AES measurement algorithm with concentration ratio calibration is shown in the Fig. 1.

1 – Formulation of the analytical problem (the silicate analysis in this case).

2 – Selection of the directional method (scheme) of sample preparation. In well-known procedures of geological and technical materials analysis, three sample preparation methods are mainly used [4]:

• dissolution in a mixture of acids in open systems when heated;

• alkaline fusion with flux in platinum dishes;

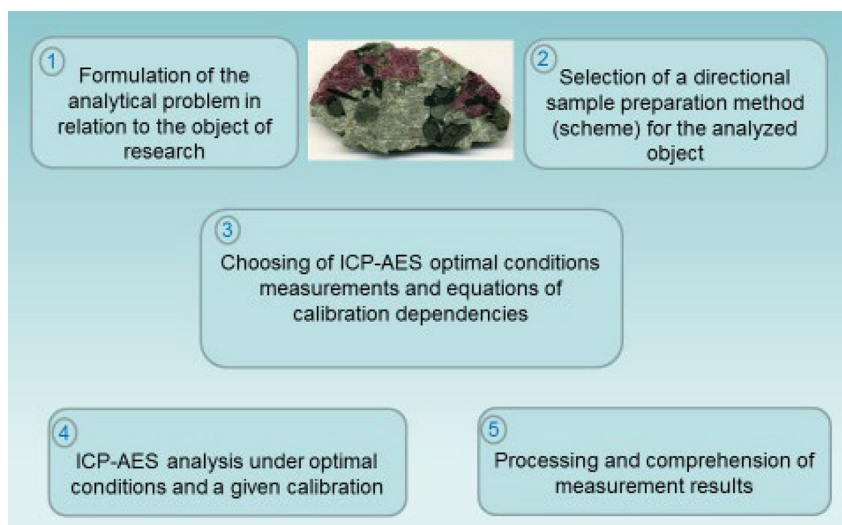• acid dissolution in autoclaves in resistive and microwave heating options.

Fig. 1. The algorithm of ICP-AES measurements with concentration ratio calibration

For instance in the certified ICP-AES procedure of silicate and carbonate rocks analysis, the sample is transferred to a solution by alkaline fusion with flux (a mixture of lithium carbonate and boric acid) in platinum crucibles in a muffle furnace at 970 ºC, with subsequent leaching of melt with hydrochloric acid [5]. This sample preparation option does not look ideal: an excessive samples dilution, platinum dishes must be used, boron spectral interference in the wavelength region 166–230 nm is observed, as well as the duration of the procedure (up to a day).

To eliminate the above disadvantages, an upgraded method based on acid dissolution of samples in closed teflon tubes-autoclaves heated in the HotBlock 200 system was proposed (Table 1).

The Scheme 1 provides complete dissolution of iron ore samples at temperatures of 150–180 ºC during 60 minutes.

For geological rocks with silicate and carbonate matrices, sample preparation is carried out in two stages (Scheme 2). This scheme afterwards proved its effectiveness when performing serial analyses, providing a full cycle of dissolution of 54 samples within 4 hours.

A fusion method with lithium hydroxide in silver crucibles heated in the HotBox 300 system has been developed for difficult-to-dissolve materials on a geological basis (ilmenite, zirconium concentrates, and refractories). Compared with the popular option of fusion with lithium metaborate in platinum crucibles [14], this method (Scheme 3) has a number of advantages:

• the cost of crucibles is significantly less;

due to the absence of boric acid, the stage of melt leaching is simplified, the level of spectral overlays is reduced, it becomes possible to determine impurity boron in the analyzed materials.

3 – Selection of optimal conditions of ICP-AES measurements and equations of calibration dependencies. The internal standard (Sc, In, Y) is most often used in ICP-AES analysis [4]. Its use in comparison with calibration in absolute intensities, as a rule, leads to an increase in the accuracy of measurements. At the same time, in the analysis of geological materials, when determining elements in the ranges content of 50–100 %, this technique turns out to be insufficient, and then a very labor-intensive method of limiting standards is used [15].

Table 1. Sample preparation of geological and technical materials

Object of analysis	Sample preparation conditions
Iron ore raw materials	Scheme 1 – acid dissolution Sample weight 0.1 g Reaction mixture: HCl (8 cm^3), HF (0.5–2 cm^3), HNO$_3$ (0.5 cm^3) Heating at 150–180 °C – 60 min
Geological materials with silicate and carbonate matrices	Scheme 2 – acid dissolution Sample weight 0.1 g Heating at 180 °C – 60 min Stage 1. Reaction mixture: HNO$_3$ (5 cm^3), HF (0.1–0.8 cm^3) Stage 2. Reaction mixture: HCl (5 cm^3), 4 % H$_3$BO$_3$ (7 cm^3) Heating at 120 °C – 20 min
Ilmenite, zircon concentrates, refractories	Scheme 3 – fusion with LiOH Sample weight 0.1 g Weight of LiOH 1 g Fusion at 720–820 ºC – 20 min Leaching of melt: 70 cm^3 HCl (1:5), HF (0.1–0.25 cm^3)

In the method with concentration ratio calibration, the matrix component of the sample acts as an internal standard. The calibration dependencies are plotted in the coordinates «relative intensity» (the ratio of signal intensities of the element being determined and the standard) – «the ratio of concentrations of the component being determined and the standard». The quantity of calibration dependencies coincides with the quantity of detectable components in the sample. In the presence of undetectable analytes, the calculations of the component contents in the samples must be adjusted. Table 2 shows the equations with concentration ratio calibration, which ensure the best accuracy of ICP-AES measurements during silicate analysis in comparison with other calibration methods [8]. It should be clarified that this calibration method has been tested in the ICP-AES analysis of geological and technical materials with F and CI contents of no more than 0.1 % by weight.

4 – ICP-AES analysis under specified conditions of sample preparation and calibration. The procedures of ICP-AES analysis of geological materials with silicate, carbonate matrices, iron ores and technical materials with improved metrological characteristics have been developed. Table 3, as an example, shows comparative accuracy indicators of ICP-AES and SCAM No. 487-HS procedures of analysis of silicate rocks.

5 – Processing and comprehension of measurement results. The ICP-AES procedure of silicate rocks analysis has successfully passed certification and is currently functioning in the Analytical Center of SC «Siberian PGO» Rosgeologiya in the rank of the standard of the enterprise STP No. 04-KHA.

The procedure iron ores analysis by ICP-AES allows to determine iron with a given, and all other components, as a rule, with accuracy exceeding GOST 23581 and in wider contents ranges [10].

The ICP-AES procedure of carbonate rocks analysis was successfully tested during the interlaboratory certification of the standard sample of slag Sh17 produced by CJSC «Institute of Standard Samples» (Yekaterinburg) [9].

Table 2. Graduation equations with concentration ratio calibration

Object Of analysis	Graduation equations for ICP-AES analysis of geological and technical materials
Silicate rocks	$$\frac{C_{Al_2O_3}}{C_{SiO_2}} + \frac{C_{Fe_2O_3}}{C_{SiO_2}} + \cdots + \frac{C_{ZrO_2}}{C_{SiO_2}} = \frac{100\ \% - \text{п. п. п.}}{C_{SiO_2}} - 1$$
Materials with a carbonate matrix	$$\frac{C_{Al_2O_3}}{C_{CaO}} + \frac{C_{Fe_2O_3}}{C_{CaO}} + \cdots + \frac{C_{ZrO_2}}{C_{CaO}} = \frac{100\ \% - \text{п. п. п.}}{C_{CaO}} - 1$$
Iron ore raw materials'	$$\frac{C_{Al_2O_3}}{C_{Fe_2O_3}} + \frac{C_{CaO}}{C_{Fe_2O_3}} + \cdots + \frac{C_{ZnO_2}}{C_{Fe_2O_3}} = \frac{100\ \% - \text{п. п. п.}'}{C_{Fe_2O_3}} - 1$$
Zircon, ilmenite concentrates, refractories with a high Mg content	$$\frac{C_{SiO_2}}{C_{ZrO_2}} + \frac{C_{HfO_2}}{C_{ZrO_2}} + \cdots + \frac{C_{TiO_2}}{C_{ZrO_2}} = \frac{100\ \% - \text{п. п. п.}}{C_{ZrO_2}} - 1$$ $$\frac{C_{Al_2O_3}}{C_{TiO_2}} + \frac{C_{CaO}}{C_{TiO_2}} + \cdots + \frac{C_{ZrO_2}}{C_{TiO_2}} = \frac{100\ \% - \text{п. п. п.}}{C_{TiO_2}} - 1$$ $$\frac{C_{Al_2O_3}}{C_{MgO}} + \frac{C_{CaO}}{C_{MgO}} + \cdots + \frac{C_{ZrO_2}}{C_{MgO}} = \frac{100\ \% - \text{п. п. п.}}{C_{MgO}} - 1$$

*) The amount of oxygen required for the oxidation of iron (II) into iron (III) oxide is taken into account in the п.п.п′.

Table 3. Data of silicate rocks analysis accuracy obtained using the ICP-AES developed procedure and SCAM 487-HS

Measurement ranges of element oxides (% wt.)	Accuracy rate (±Δ,%)		Measurement ranges of element oxides (% wt.)	Accuracy rate (±Δ,%)	
	ICP-AES	SCAM № 487-HS		ICP-AES	SCAM № 487-HS
SiO$_2$			K$_2$O		
from 20,0 to 30 incl.	2,0	3,7	from 0,1 to 0,2 incl.	20,0	37,0
over 30,0 to 40,0 incl.	2,0	2,5	over 0,2 to 0,5 incl.	20,0	29,0
over 40,0 to 50,0 incl.	2,0	2,0	over 0,5 to 1,0 incl.	8,0	25,0
over 50,0 to 60,0 incl.	1,4	1,6	over 1,0 to 2,0 incl.	8,0	21,0
over 60,0 to 70,0 incl.	1,2	1,4	over 2,0 to 5,0 incl.	8,0	16,0
over 70,0 to 95,0 incl.	1,2	1,4	over 5,0 to 10,0 incl.	-	11,0
CaO			TiO$_2$		
from 0,1 to 0,2 incl.	16,6	43,0	from 0,01 to 0,02 incl.	38,0	55,0
over 0,2 to 0,5 incl.	16,6	31,0	over 0,02 to 0,05 incl.	38,0	43,0
over 0,5 to 1,0 incl.	9,8	24,0	over 0,05 to 0,1 incl.	30,0	33,0
over 1,0 to 2,0 incl.	9,8	19,0	over 0,1 to 0,2 incl.	12,0	27,0
over 2,0 to 5,0 incl.	9,8	14,0	over 0,2 to 0,5 incl.	12,0	22,0
over 5,0 to 10,0 incl.	7,3	10,0	over 0,5 to 1,0 incl.	9,0	18,0
over 10,0 to 20,0 incl.	3,3	6,0	over 1,0 to 2,0 incl.	6,0	14,0
over 20,0 to 30,0 incl.	1,9	5,0	over 2,0 to 5,0 incl.	6,0	11,0
over 30,0 to 40,0 incl.	-	3,0	over 5,0 to 10,0 incl.	-	7,0
MgO			Al$_2$O$_3$		
from 0,1 to 0,2 incl.	35,0	43,0	from 0,2 to 0,5 incl.	13,0	35,0
over 0,2 to 0,5 incl.	30,0	31,0	over 0,5 to 1,0 incl.	13,0	27,0
over 0,5 to 1,0 incl.	20,0	24,0	over 1,0 to 2,0 incl.	7,0	22,0
over 1,0 to 2,0 incl.	4,5	18,0	over 2,0 to 5,0 incl.	7,0	17,0
over 2,0 to 5,0 incl.	4,5	13,0	over 5,0 to 10,0 incl.	3,0	13,0
over 5,0 to 10,0 incl.	4,5	9,0	over 10,0 to 20,0 incl.	3,0	7,0
over 10,0 to 20,0 incl.	2,0	7,0	over 20,0 to 30,0 incl.	2,0	5,0
over 20,0 to 30,0 incl.	2,0	5,0	over 30,0 to 40,0 incl.	-	4,0
over 30,0 to 40,0 incl.	2,0	4,0	over 40,0 to 50,0 incl.	-	3,1
over 40,0 to 50,0 incl.	-	3,0	over 50,0 to 60,0 incl.	-	2,7
Fe$_2$O$_3$			MnO		
from 0,5 to 1,0 incl.	10,0	26,0	from 0,01 to 0,02 incl.	30,0	53,0
over 1,0 to 2,0 incl.	10,0	20,0	over 0,02 to 0,05 incl.	30,0	45,0
over 2,0 to 5,0 incl.	10,0	14,0	over 0,05 to 0,1 incl.	19,0	39,0
over 5,0 to 10,0 incl.	4,0	8,0	over 0,1 to 0,2 incl.	10,0	27,0
over 10,0 to 20,0 incl.	4,0	4,0	over 0,2 to 0,5 incl.	10,0	20,0
over 20,0 to 30,0 incl.	3,0	3,0	over 0,5 to 1,0 incl.	4,0	-
over 30,0 to 40,0 incl.	-	2,0	over 1,0 to 2,0 incl.	4,0	-
P$_2$O$_5$			Na$_2$O		
from 0,01 to 0,02 incl.	23,0	37,0	from 0,5 to 1,0 incl.	13,0	-
over 0,02 to 0,05 incl.	23,0	29,0	over 1,0 to 2,0 incl.	13,0	20,0

Table 3 Continued

Measurement ranges of element oxides (% wt.)	Accuracy rate (±Δ,%)		Measurement ranges of element oxides (% wt.)	Accuracy rate (±Δ,%)	
	ICP-AES	SCAM № 487-HS		ICP-AES	SCAM № 487-HS
over 0,05 to 0,1 incl.	23,0	24,0	over 2,0 to 5,0 incl.	8,4	16,0
over 0,1 to 0,2 incl.	8,0	19,0	over 5,0 to 10,0 incl.	8,4	11,0
over 0,2 to 0,5 incl.	8,0	15,0	over 10,0 to 12,0 incl.	8,4	-
over 0,5 to 1,0 incl.	8,0	12,0			
over 1,0 to 2,0 incl.	5,0	9,0			
over 2,0 to 5,0 incl.	5,0	-			

Using the ICP-AES procedure of technical materials analysis, additional information on the state standard samples composition of ilmenite (GSO 8850–2006), zircon (GSO 4087–87) concentrates, and chromite-periclase type refractory HPZ (GSO 4117–87) was obtained [11].

Conclusion

Based on the conducted research, as well as the results obtained by testing the developed procedures on real objects, it can be argued that the ICP-AES method with concentration ratio calibration can be used in full-scale silicate analysis of geological and technical materials.

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