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Determination of Au, Pb, Ni and Co in mineral raw materials by atomic absorption spectroscopy with graphite furnace

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Abstract

A method for quantitative determination of gold, lead, nickel, cobalt in a range of concentrations from mg/g to ng/g was proposed. Method consists of annealing, treatment with acids followed by extraction. Determination of nickel, cobalt and lead was carried out after the decomposition of the sample, without discharge of the sample matrix. Method was tested by certified reference material and various rock samples. Method can be applied for determination of corresponding metals in ores, rocks and waste mining industry.

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Keywords: Atomic absorption spectroscopy; gold; cobalt; lead; nickel.

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1. Introduction

Quantitative determination of gold, lead, nickel and cobalt in rocs is a complex issue related to the decision of a number of practical problems. There is the selection of the analysis method and the development of effective decomposition methods for rocks and separation of determined impurity. Currently, in order to solve this problem several methods are used such as neutron activation analysis, inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS) [1-5].

Atomic absorption spectroscopy (AAS) is widely used for analysis of different types of natural objects, both in industrial and scientific purposes. AAS is characterized by low-cost equipment and high -efficiency in the single element determination[3]. Method of flame atomic absorption spectroscopy (FAAS) allows to define the elements in the concentrations mg/g, and the use of electrothermal atomization graphite furnace increases the range to ng/g.

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Decomposition of rock was conducted in two ways: by fusion with inorganic salt(Na_2CO_3, $LiBO_2$, $KHSO_4$ и KHF_2) or dissolved in mineral acids(HNO_3, H_2SO_4, $HClO_4$, HCl)[6].

In case when the determination of the silicon concentration was not performed, it is necessary to use the method of dissolving acids as less time-consuming. To increase the sensitivity of the method to concentrations ng/g, it is necessary to carry out separation of the analyte with extraction. For this purpose we have chosen the method of gold extraction by alkyl sulfides in toluene from chloride solutions[7]. Di-n-octyl sulfide is selected as a high-capacity and selective extraction agent for gold and platinum group metals[8].

2. Experimental

We used a set of AAS VARIAN AA 240 DUO, which includes flaming VARIAN 240F and electrothermal VARIAN 240AZ spectrometers. For electrothermal atomizer we used graphite cuvette VARIAN, ultra high purity nitrogen was used as the carrier gas. Voltammetric measurements were carried out with the analyzer TA-4 (“Tom’analit”, Tomsk) with polyethylene impregnated graphite electrode. As a reference electrode, silver/silver chloride electrode was used. Calibration solutions of gold, lead, nickel, and cobalt were obtained by diluting the standard samples obtained from Sigma. Nitric, hydrofluoric and hydrochloric acids were purchased ultrapure quality and sub boiled by Milestone SubPur systems, di-n-octyl sulfide CAS № 2690-08-6 obtained from Sigma.

2. Result and Discussion

We used rocks from Altai-Sayan folded area, samples were prepared by grinding to the particle size of 200 microns. Ore charge 1 g was placed in a corundum crucible and was claimed in a muffle furnace at the temperature 600-650^{0}C for an hour. The sample was cooled down in the air, then 15 ml of hydrofluoric acid was added and evaporated on electric furnace at the temperature 180^{0}C to wet residue. Freshly prepared aqua sample (15 ml) was added to the residue, the mixture was evaporated up to the volume of 2-4ml at 180^{0}C. Then concentrated hydrochloric acid (10 ml) was added to the mixture, it was evaporated up to the volume 2-4 ml at the temperature 100^{0}C. After mixture was cooled and diluted up to the volume of 10 ml of 4M hydrochloric acid. In order to concentrate gold, we extracted obtained aqueous solution with 1 ml of 5 % di-n-octyl sulfide in toluene[9]. High sensitivity of method allows carrying out determination of lead, nickel and cobalt without preliminary extraction[10]. Method was controlled by measurement of the gold and lead concentration in reference materials(RM)(table 1)

Table 1. Results of gold determination in reference materials (n=10, P=0.95)

	Objects of analysis	**Gold content, (mg/g)**	**Gold content by AAS with electrothermal atomization (mg/g)**
1	RM № 8770-2006 РМК 4	0.45	(0.35±0,09)
2	RM № 8771-2006 РМО 5	1.4	(1.10±0,29)
3	RM № 8773-2006 РВ 3-8	0.21	(0.17±0,05)

These data demonstrate the possibility of developed for the gold analysis in ores technique employment. Accuracy of determination does not exceed 28%.

Table. 2 shows the data of gold content in the analyzed samples of rocks from Altai-Sayan folded area determined by AAS with electrothermal atomization after its discharge from the extraction of the sample matrix. Correctness of conducted determinations was controlled by comparison of the determination results with the data obtained by anodic stripping voltammetry.

Table 2. Results of gold determination in rocks from Altai-Sayan folded area. (n=10, P=0.95)

№	Objects of analysis	Gold content by AAS with electrothermal atomization (mg/g)	Gold content by by stripping voltammetry (mg/g)
1	Granites	(1.7±0.4)	(1.5±0.4)
2	Pyroxene gneisses	(2.2±0.5)	(2.4±0.6)
3	Breccias	(1.3±0.3)	(1.2±0.3)
4	Cataclasites	(5.3±1.4)	(5.1±1.3)

Simultaneous presence of lead, nickel and cobalt does not obstruct the determination of these elements as their spectral lines are not overlapped with each other, therefore the spectral interference can be ignored. Correctness of the methodology was verified by comparison of obtained results with the data obtained by electrothermal atomization AAS of the reference materials (Table 3)

Table 3. Results of lead determination in reference materials (n=10, P=0.95)

	Objects of analysis	certified values lead, (mg/g)	Lead content by AAS with electrothermal atomization (mg/g)
1	RM № 8770-2006 PMK 4	7.5	(6.7±1.7)
2	RM № 8771-2006 PMO 5	16.0	(14.3±2.9)
3	RM № 8773-2006 PB 3-8	4.9	(4.1±1.1)

These data demonstrate the possibility of developed for the gold analysis in ores technique employment. Accuracy of determination does not exceed 28%.

Determination of lead, nickel and cobalt in rocks from Altai-Sayan folded area was carried out without separation of them from the sample matrix and with aqua sample digestion. After this we obtained results of analysis by two methods: AAS with electrothermal atomization and the flame atomization (Table 4).

Table 4 Results of lead, cobalt and nickel determination in rocks from Altai-Sayan folded area

№	Objects of analysis	Elements content by AAS with electrothermal atomization (mg/g)			Elements content by AAS with flame atomization (mg/g)		
		Pb	Ni	Co	Pb	Ni	Co
1	Granites	(6.7±1.7)	(1.4±0.4)	(0.92±0.24)	(6.2±1.5)	(1.27±0.3)	(0.79±0.22)
2	Pyroxene gneisses	(3.1±0.7)	(3.2±0.8)	(1.4±0.4)	(2.9±0.8)	(2.9±0.7)	(1.6±0.4)
3	Breccias	(1.8±0.4)	(1.8±0.4)	(2.1±0.5)	(1.6±0.4)	(1.5±0.4)	(1.8±0.5)
4	Cataclasites	(4.5±1.1)	(2.9±1.0)	(1.8±0.5)	(3.9±1.1)	(2.3±0,5)	(1.7±0.4)

There are not significant differences in results of metals determination in the same samples. This fact indicates the correctness of both methods for determination of listed metals.

3. Conclusion

A simple and effective method of rocks with different composition and elements content opening was developed. This technique was verified on the reference materials samples. The accuracy of elements determination does not exceed 28 % for Au and 30% for Pb, Ni and Co without separation of the sample matrix. Developed procedure shows high convergence in the determination of analyzed elements.

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