

IMPROVING THE ASSAY-GRAVIMETRIC METHOD FOR DETERMINING THE CONTENT OF NOBLE METALS

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The study considers the current state and problems of analytical control as the most important component of all stages of technology and production of noble metals. Based on the analysis carried out, a universal method for measuring the mass fraction of gold and silver in ores, products of their enrichment and metallurgical processing by the assay-gravimetric method was improved, and the optimal parameters for determining gold and silver were determined.

Keywords: noble metals, assay-gravimetric method, gold, silver, charge

INTRODUCTION

Regular determination of the content of precious metals is an essential condition for the analytical control of gold recovery production. The lack of a unified regulatory framework for the methods of analysis of raw materials and processed products containing precious metals leads to disputable situations between miners, processors and refineries.

The analysis of national and foreign regulatory documents showed that the mass analysis of materials for the determination of gold and silver contents is carried out by modern instrumental methods - atomic absorption [1, 2], atomic emission with inductively coupled plasma [3, 4, 5], as well as intruding energy-dispersive X-ray spectral fluorescence [6, 7].

The disadvantages of using instrumental methods without preconcentration are: low representativeness of samples when taking a small sample for the purpose of subsequent transfer to a noble metal solution, incomplete decomposition of individual minerals with acids, and the need to determine the content of gold and silver using separate methods.

To eliminate these shortcomings, assay-atomic-absorption and assay-atomic-emission methods for the determination of noble metals with complete or incomplete cupellation were developed.

Due to the accuracy of the determination of noble metals, the assay-gravimetric method of analysis re-

mains in demand as a control and arbitration method, despite the duration of its implementation and high cost compared to instrumental methods.

Assay analysis is a method for quantitative determination of the content of noble metals, mainly gold and silver, in ores, products of their enrichment and metallurgical processing, waste, alloys, products and other materials, based on the property of noble metals to dissolve well in molten lead with the formation of fusible alloys. Assay analysis usually uses large (representative) weights of a substance, which makes it possible to determine the content of noble metals even in relatively poor materials.

The assay melting method has been known since ancient times and has not lost its practical significance to this day. For a long time, the ability to determine gold and silver by the assay method was considered an art [8]. Assay art, being a branch of metallurgy, developed in parallel with the latter, and its beginning is as difficult to indicate as the beginning of metallurgy itself.

The peculiarity of assay analysis is that noble metals in this case are determined without their preliminary separation from other components that make up the analyzed material.

The assay method still does not have a complete theoretical justification, although the metrological part of assay melting has been worked out quite well.

According to the literature, ores and products containing a significant amount of impurities that impede smelting (arsenic sulfide with a high iron content) require special preliminary preparation. To determine gold and silver in sulfide arsenic ores and technological products, oxidative low-temperature roasting or oxidative roasting with soda is recommended, followed by aqueous leaching of the arsenic-sodium salt formed during roasting [9], or treatment with sulfuric acid [10].

M.S. Zharlikov, Affiliate of RSE National Center on Complex Processing of Raw Materials of the Republic of Kazakhstan «VNIItsvetmet», Ust-Kamenogorsk, Kazakhstan
R.A. Aubakirova, Sh.K. Sanyazova, S. Amanzholov East Kazakhstan University, Ust-Kamenogorsk, Kazakhstan
G.K. Daumova (gulzhan.daumova@mail.ru), E.N. Ivashchenko. B.S. Saurbayeva, D. Serikbayev East Kazakhstan Technical university, Ust-Kamenogorsk, Kazakhstan

The disadvantages of the recommended methods are: their duration, high probability of mechanical losses and losses through volatilization.

The presence of large amounts of iron in samples leads to underestimated, poorly reproducible results in the determination of gold and silver, which is caused by the infusibility of its compounds. The increased viscosity of the slag slows down the settling of drops of molten lead. In addition, iron oxide formed during the decomposition of arsenopirite and pyrite causes emulsification of molten lead, because of which, during the melting time, it does not have time to fully collect and settle to the bottom of the crucible [9].

The presence of large amounts of copper, zinc, sulfur and other components that are difficult to slag requires the use of highly caustic slags in assay melting, which leads to rapid corrosion of assay glassware and often leads to loss of samples during analysis.

To open successfully a sample by assay melting, the following is required:

- 1 Observe the optimal mass ratio of the flux components and the sample to ensure complete decomposition of the sample and obtain a liquid melt of slag, which, after cooling, should be easily separated from the collector.
- 2 Grind the sample and charge components to 0,074 mm (sometimes up to 0,044 mm) to ensure closer contact between the collector and noble metals.
- 3 Melting should be carried out at a temperature of about 950 °C - 1100 °C for 0,5 – 1,5 hours with a slight overheating at the end of the process to deposit the collector on the bottom of the crucible.

If, during the analysis, it is not possible to provide conditions for successful opening of the sample, then they resort to additional extraction of noble metals: remelting of slags with an additional portion of the collector, washing of slags, etc. All additional operations lead to an increase in time, energy and labor costs analysis.

MATERIALS AND METHODS

Research has been carried on the development of a methodology for measuring the mass fraction of gold and silver in ores, products of their enrichment and metallurgical processing by assay-gravimetric method.

This study was carried out in order to select the optimal parameters: sample size, charge composition and temperature regimes, in order to obtain the best gold and silver recovery rates for a large number of materials under study, as well as extended ranges for determining elements.

57 samples were used to conduct research to assess the quality indicators of measurement technique: oxidized ore, sulfide ore, flux ore, gold ore, dump tailings, cleaning tailings, table tailings, amalgamation tailings, cyanidation tailings, drain, slag, flotation feed, mill feed, BIOX feed, CIL feed, flotation concentrate, clean-

ing concentrate, gold concentrate; with the content of gold and silver in the range of mass fractions:

- gold from 0,2 ppm to 500,0 ppm;
- silver from 10,0 ppm to 1 000,0 ppm.

Experimental studies were carried out under normal conditions with:

- ambient air temperature (20 ± 5) °C;
- relative air humidity not more than 80 %.

RESULTS AND DISCUSSION

The following requirements were taken into account when choosing a sample and the composition of the charge for assay melting:

- the components of the charge must be selected in proportions that ensure the production of a fluid slag and a mass of 30-50 g of workpiece;
- the mass of the gold-silver bead should not exceed 30-50 mg;
- with a low silver content, it is necessary to conduct a control experiment (check) to account for losses during cupellation.

The conducted studies have shown the feasibility of using a mixture of composition, g: sample - 10-50, litharge - 75-100, soda - 65, borax - 25, coal or saltpeter, depending on the reducing ability of the analyzed material.

The proposed charge composition and analysis conditions do not require special preliminary preparation, while the most complete extraction is achieved; the analysis results are highly accurate and reproducible.

The result was the development of a universal method for measuring the mass fraction of gold in the range from 0,2 ppm to 500,0 ppm and silver from 10,0 ppm to 1 000,0 ppm in ores, their enrichment products and metallurgical processing by assay-gravimetric method.

For the first time in the measurement technique, it is indicated that when only gold is determined in a sample, the required amount of silver is added when weighing sample portions in the form of metallic silver.

Studies of the metrological characteristics of the measurement technique were carried out in accordance with the requirements:

- ST RK 2.18-2009 “GSI RK. Measurement techniques. Procedure for development, metrological certification, registration and application”;
- Procedure for development, metrological certification, registration and application”– GOST 8.010-2013 “GSI. Measurement techniques. Basic Provisions”;
- RMG 61-2010 “GSI. Indicators of accuracy, correctness, precision of methods of quantitative chemical analysis. Evaluation Methods”;
- GOST ISO 5725-6-2003 Accuracy (correctness and precision) of measurement methods and results. Part 6. Using precision values in practice.

The measurement technique ensures the performance of measurements with the assigned error characteristics at a confidence level $P = 0,95$, given in Table 1.

Table 1 Characteristics of the error at the confidence level $P = 0,95$

In ppm

Element	Mass fraction of the element	Repeatability index (standard deviation of repeatability)/ σ_r	Index of intralaboratory precision (standard deviation of intralaboratory precision) / σ_{R_i}	Accuracy indicator (absolute error limits)/ $\pm \Delta$
Gold	0,2-0,5	0,03	0,06	0,1
	0,5-1,0	0,12	0,12	0,3
	1,0-2,0	0,18	0,21	0,5
	2,0-4,0	0,30	0,36	0,9
	4,0-8,0	0,45	0,51	1,2
	8,0-15,0	0,60	0,66	1,6
	15,0-30,0	0,91	0,91	2,1
	30,0-60,0	1,81	1,96	4,6
	60,0-120,0	2,42	2,56	6,0
	120,0-250,0	3,02	3,02	7,1
250,0-500,0	5,80	6,04	14,2	
Silver	10,0-20,0	1,21	1,60	3,8
	20,0-40,0	2,42	2,71	6,4
	40,0-80,0	3,78	3,93	9,2
	80,0-150,0	4,62	4,92	11,6
	150,0-300,0	7,73	8,07	19,0
	300,0-600,0	12,08	12,08	28,4
	600,0-1 000,0	15,2	15,20	35,7

Note: The established numerical values of the absolute error limits correspond to the numerical values of the expanded uncertainty U with a coverage factor $k = 2$.

Table 2 Standards for operational control with a confidence level $P = 0,95$

In ppm

Element	Mass fraction of the element	Repeatability limit (the value of the allowed discrepancy between the results of three parallel determinations)/ r	Limit of intralaboratory precision (the value of the allowable difference between two results of the analysis obtained under conditions of intralaboratory precision)/ R_i
Gold	0,2-0,5	0,1	0,2
	0,5-1,0	0,4	0,4
	1,0-2,0	0,6	0,7
	2,0-4,0	1,0	1,2
	4,0-8,0	1,5	1,7
	8,0-15,0	2,0	2,2
	15,0-30,0	3,0	3,0
	30,0-60,0	6,0	6,5
	60,0-120,0	8,0	8,5
	120,0-250,0	10,0	10,0
250,0-500,0	19,2	20,0	
Silver	10,0-20,0	4,0	5,3
	20,0-40,0	8,0	9,0
	40,0-80,0	12,5	13,0
	80,0-150,0	15,3	16,3
	150,0-300,0	25,6	26,7
	300,0-600,0	40,0	40,0
	600,0-1 000,0	50,3	50,3

To assess the precision indicators (repeatability, intralaboratory precision and reproducibility) in accordance with the requirements of the measurement technique, 20 analysis results ($L=20$) of working samples were obtained for 11 subranges of the mass fraction of gold and 7 sub-

ranges of the mass fraction of silver; for intermediate intervals, the method of linear interpolation was used.

To assess the correctness index, 10 analysis results ($L=10$) of working samples and samples with a modified sample were obtained.

Processing of research results was carried out according to RMG 61-2010 GSI. Indicators of accuracy, correctness, precision of methods of quantitative chemical analysis. Evaluation Methods.

The uncertainty assessment was carried out in two ways in accordance with RMG 43-2001 GSI. Application of the “Guidelines for the Expression of Uncertainty in Measurements” and the EURAHIM/CITAC Guidelines “Quantifying Uncertainty in Analytical Measurements”.

The standards for operational control of the analysis method are presented in Table 2.

Operational control standards (Table 2) show a direct relationship between the mass fraction of gold and silver on the limit of repeatability and the limit of intralaboratory precision.

The use of these measurement methods for analytical control ensures the reliability of information on the composition of samples of the metallurgical stage and improves the quality of products.

CONCLUSION

The products of metallurgical processing are characterized by a variety of chemical compositions in a wide range of contents of the determined elements. At the same time, the well-known methods of analysis used in analytical control have not lost their relevance and ensured wide application.

This article shows the prospects for improving the assay-gravimetric method for determining the contents of gold and silver in ores, products of their enrichment and metallurgical processing.

Consideration of the state and problems of analytical control in the production of precious metals shows its great importance at all stages of technology and practical application.

Discrepancies, compared with other methods for determining noble metals, allow us to recommend it for use as a control and arbitration.

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