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ATOMIC EMISSION METHOD WITH INDUCTIVELY COUPLED PLASMA FOR DETERMINING OF NOBLE METALS (Au, Ag) IN SAMPLES OF INDUSTRIAL BLISTER COPPER

Abstract. In the article weare presenting the results of investigation of AES ISP method for Au and Ag determination in samples of industrial blister copper. The developed method allows determining Au in the range 28-56 g/ton, Ag – 2000-3000 g/ton. Control of precision was conducted using control analytical method (assay-gravimetric) as well as using measurement of state standard sample of copper content with attested values of impurities. The developed method is not inferior in metrological characteristics to control analytical method. Optimal spectral lines for Au – 242,795 nm and for Ag – 328,068 nm were selected because they have the most sensitivity and do not have spectral noises. Statistical processing of calibration characteristics for AES ISP determination of Ag and Au was conducted in accordance to RIS 54-2002. As a result, values of average standard relative deviations, the ratio of the average squared deviations and quantile of distribution were obtained. Parameters of precision, correctness, repeatability, reproducibility of the method were calculated according to RIS 61-2013.

Keywords: blister copper, noble metals, melting, gold, silver, atomic emission, inductively coupled plasma.

Introduction

Kazakhstan copper, as well as aluminum, nickel and ferrous metals, is one of the main export goods. Copper presents on market as copper concentrate, refined copper and copper wire rod.

Blister copper contains impurities, which deteriorate quality of copper (sulfur, oxygen et al.), and therefore to be removed, as well as impurities non-affecting the quality of copper, but extracted because of their value (silver and gold) [1-4].

In present time for determination of gold and silver content in samples of blister copper of copper production assay-gravimetric method of analysis is widely used [5-9]. Related to bulk up of copper production necessary of using more express method of analysis emerges not giving up by accuracy to assay-gravimetric method. Thus, the development and implementation of appropriate methods of blister copper analysis is an important issue.

Methods and materials

Development of the method of determination of noble metals (Au, Ag) in industrial blister copper samples includes following stages [10-13]:

1) investigation of influence of sample preparing stage and measuring on the analysis result;

1) making of calibration characteristics and their statistical processing;

2) description of the AES ICP method of impurities content determining in samples of copper production;

3) metrological substantiation of the developed measurement procedure.

Results and Discussion

The calibration characteristics for determination of noble metals impurities content by the atomic emission method were built using certified mixtures prepared from pure metals in accordance with the method of measures performing [10, 11].

From scientific literature it is known that for determination of Au and Ag analytical spectral lines are used, which bands lengths are represented in Table 1.

Table 1 - Analytical spectral lines for determination of Au and Ag content using AES ICP method

Determined element	Band width
Au	242,795/267,595 nm
Ag	328,068/338,289 nm

We have selected the most optimal spectral lines for building of calibration characteristics for gold – 242,795 nm, and for silver – 328,068 nm. These lines are the most sensitive and do not have spectral interferences.

The initial data necessary for building of calibration characteristics are represented in Table 2.

Table 2 - The results of AES ICP determination of Au and Ag in calibration solutions

C_{Me} mg/l	$I_{imp/sec}$	
	Ag (328,068 nm)	Au (242,795 nm)
Blank	22042,9	5038,77
PC-1	681869	16094,4
PC-2	1217090	25561,5
PC-3	2345950	44945,3

where I – the average value of intensity of analytical signal of the metal, imp/sec

C_{Me} – content of the metal in calibration solution, mg/l (Table 3)

Table 3 - Concentrations of comparative solution

Comparative solution	Concentration, mg/l	
	Ag	Au
PC-1	10,0	0,5
PC-2	20,0	1,0
PC-3	40,0	2,0

Intensity of analytical signal (number of impulses per second) was measured triple for each element and for each calibration solution. Using obtained values calibration characteristics have been built. The characteristics represent dependence of analytical signal intensity on analyte content in calibration solutions (mg/l). Calibration characteristics are represented on Figures 1 and 2.

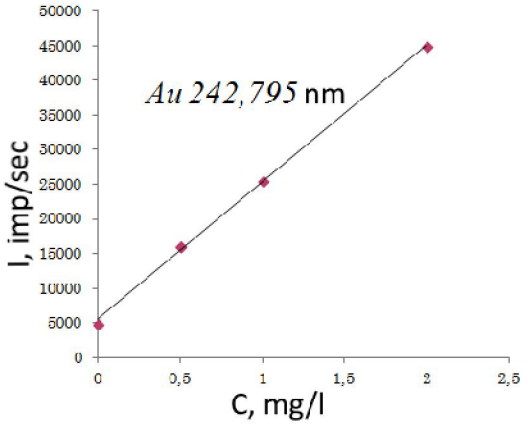

Figure 1 - Dependence of analytical signal intensity on Au concentration

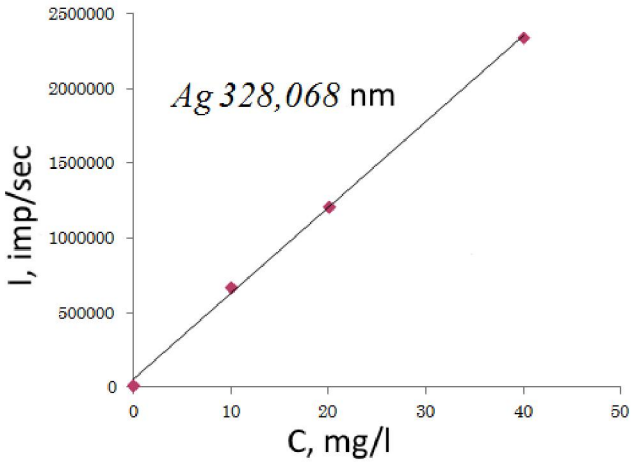

Figure 2 - Dependence of analytical signal intensity on Ag concentration

According to the Recommendations on interstate standardization 54-2002 «Calibration characteristics of means of measurement of composition and properties of substances and materials. Measurement procedure with the use of reference materials» (RIS 54-2002) statistical calculation of built calibration characteristics has been performed. As a result of statistical calculations of calibration characteristics for determination of Ag and Au values of average standard relative deviation, standard deviations of coefficients a and b, relation of average squares of the deviation and quantile of distribution were obtained. The results are represented in Table 4. Statistical processing of the results of calibration characteristics were conducted using the least squares methodas far as arithmetic mean value of relative standard deviations $\overline{\gamma} \leq 0{,}4$ [14].

Table 4 - Results of statistical processing of calibration characteristic for AES ICP determination of Au and Ag

Analyte	γ	a	S_a	b	S_b	V_y	$F(V_1, V_2)$
Ag	0,011	2,20	8,35	6,31	1,36	4,22	4,77
Au	0,002	5,04	2,59	2,08	2,69	4,31	

γ – average value of relative standard deviation; a and b – coefficients in equation γ = a + bx; S_a, S_b – standard deviations of coefficients a and b; V_y – relation of average squares of deviations; F – quantile of distribution.

Table 5 - Published data of the calibration standard sample (VSM 1.3) content

Element	Index of Standard sample									
	VSM1.3-1	VSM1.3-2	VSM1.3-3	VSM1.3-4	VSM1.3-5	VSM1.3-6	VSM1.3-7	VSM1.3-8	VSM1.3-9	VSM1.3-10
	Mass fraction of elements, %									
Ag	0,094±0,005	0,293±0,005	0,00270±0,0002	0,0474±0,0023	0,0257±0,0009	0,00164±0,00015	0,00204±0,00021	0,0108±0,0008	0,105±0,008	0,0244±0,0027

Obtained value V_y is compared with the value ofquantile of distribution F [14] with the degree of freedom $V_1 = N - 2$ and $V_2 = N(I - 1)$.

As a result of mathematical processing we have obtained $V_y \leq F(V_1, V_2)$ (V_y=4,22 (Ag), V_y=4,31 (Au), F (V_1,V_2) = 4,77), which justifies the hypothesis about linearity of calibration characteristic.

For calibration of spectral equipment, we used state standard samples of blister copper with the content VSM 1.3 as represented in the Table 5.

We have determined content of Ag impurity in calibration standard sample of VSM1.3-2 set in order to define opportunities for using of the developed method for analytical control of blister copper in copper industry. The obtained results in comparison with attested values for each element are represented in Table 6.

Table 6 - The results of AES ISP determination of Au and Ag content in samples of industrial blister copper and calibration standard sample of substance content set VSM1.3(n – results number, n=3, C – an average of analysis results mg/l, S_r – relative standard deviation of analysis results, t_p – Student coefficient, t_p=0,95)

Sample index	Element	Attested analyt content, g/ton	Concentration of analyte, g/ton	S_r, %	$\delta = \pm\frac{S_r t_p}{\sqrt{n}}$,%
A-1	Ag	-	2330,2	0,008	0,021
A-2		-	2330,2	0,005	0,012
A-3		-	2923	0,004	0,011
VSM 1.3 -2		2930 ±0,005	2929,06	0,0034	0,0085
A-1	Au	-	37,25	0,002	0,0057
A-2		-	29,95	0,0017	0,0041
A-3		-	55,45	0,019	0,048

Accuracy control was performed using the control method of analysis (assay-gravimetric). The results are presented in table 7. The developed technique is not inferior in its metrological characteristics to the control method of analysis.

Table 7 - Comparison of analysis results obtained with AES ISP and assay-gravimetric methods

Sample index	Metal content, g/ton			
	AES ISP		Assay-gravimetric method	
	Au	Ag	Au	Ag
A-1	37,25	2330,20	41,30	2681,40
A-2	29,95	2330,20	30,00	2335,00
A-3	55,45	2923,00	56,60	2962,70

Ranges and subranges of determined element concentrations are presented in Table 8.

Table 8 - Determined concentration ranges of Au and Ag in samples of blister copper

	Au, g/ton	Ag, g/ton
Determined concentration ranges	28-60	2000-3000
Determined concentration subranges	28-36	2000-2300
	37-46	2301-2600
	47-60	2601-3000

Processing of accuracy characteristics of results was conducted in accordance with requirements of the Recommendations on interstate standardization 61-2003 «State system for ensuring the uniformity of measurements. Accuracy, trueness and precision measures of the procedures for quantitative chemical analysis. Methods of determination» (RIS 61-2003) [15].

For estimation of repeatability of parallel determinations of control analysis values of mean square deviations - S_{rm} and repeatability limit - r_m of corresponding subranges of components have been obtained (Table 9).

Table 9 - Parameters of repeatability for AES ISP method of determination of Ag, Au content in industrial blister copper

Element	Subranges of determined concentration, g/ton	S_{rm}	$\cdots_{rm}$	r_m
Au	28-36	0,2997	0,2997	0,8302
	37-46	0,3723	0,3723	1,0315
	47-60	0,5576	0,5576	1,5447
Ag	2000-2300	23,3751	23,3751	64,7491
	2301-2600	23,3987	23,3987	64,8146
	2601-3000	29,2317	29,2317	80,9718

For estimation of analysis method reproducibility for parallel determination of control analyses values S^2_{ml}, S_{Rm}, $G_{m(max)}$, $\cdots_{Rm}$, R_m for corresponding subranges of determined components have been obtained (Table 10).

Table 10 - Parameters of reproducibility for AES ISP method of determination of Ag, Au content in industrial blister copper

Element	Subranges of determined concentration, g/ton	S_{Rm}	$G_{m(max)}$	$\cdots_{Rm}$	R_m	$S^2_{ml} \cdot 10^{-4}$
Au	28-36	0,1237	0,4716	0,1237	0,3428	0,089
	37-46	0,1537	0,4752	0,1537	0,4258	0,014
	47-60	0,2300	0,4856	0,2300	0,6372	0,031
Ag	2000-2300	9,6465	0,4762	9,6465	26,7208	0,055
	2301-2600	9,6525	0,4819	9,6525	26,7374	0,054
	2601-3000	12,055	0,4864	12,055	33,3916	0,085

Estimation of correctness has been conducted using check method of analysis (assay-gravimetric) and through measuring of state standard sample of copper content with attested amounts of impurities.

Values of precision parameters are presented in Table 11.

Table 11 - Precision parameters for AES ISP method of determination of Ag and Au content in blister copper

Element	Subranges of determined concentration, g/ton	Repeatability (Standard sample of concentration) σ_r	Reproducibility (Standard sample of concentration) σ_R	Correctness (limits of non-excluded systematic error) $\pm\Delta c$	Precision (limit of the absolute error) $\pm\Delta$
Au	28-36	0,2997	0,123755	0,33956	0,242559
	37-46	0,3723	0,153718	0,33958	0,301288
	47-60	0,5576	0,230036	0,33958	0,450871
Ag	2000-2300	23,3751	9,646498	0,48749	18,90714
	2301-2600	23,3987	9,652491	0,57398	18,91888
	2601-3000	29,2317	12,05473	0,42777	23,62727

Conclusions

Thus, possibility of determination of Au and Ag content in samples of blister copper using AES ISP method has been revealed based on analysis of scientific and regulatory literature.

Advantages of the method are high stability of discharge radiation, high measurement speed, calibration simplicity, possibility of simultaneous multielemental determination of macro- and micro-components. Weak matrix noise caused rapid introduction this method of analysis in the workflow of many research and industrial laboratories.

At the present time assay-gravimetric method is the most used method for determination of gold and silver content in samples of blister copper in copper production. Because of increasing of copper production necessity of more express, not inferior in accuracy to assay-gravimetric analytical method is occurring.

The developed AES ISP method for Au and Ag determination in samples of industrial blister copper allows determining Au in the range 28-56 g/ton, Ag – 2000-3000 g/ton. Control of precision was conducted using control analytical method (assay-gravimetric) as well as using measurement of state

standard sample of copper content with attested values of impurities. The developed method is not inferior in metrological characteristics to control analytical method.

In the course of this research work scanning electron microscopy was used for confirmation of presence of micro- and macro-quantities of Au and Ag in the samples of blister copper.

Optimal spectral lines for Au – 242,795 nm and for Ag – 328,068 nm were selected because they have the most sensitivity and do not have spectral noises.

Statistical processing of calibration characteristics for AES ISP determination of Ag and Au was conducted in accordance to RIS 54-2002. As a result, values of average standard relative deviations, standard deviations of a and b coefficients, the ratio of the average squared deviations and quantile of distribution were obtained.

Parameters of precision, correctness, repeatability, reproducibility of the method were calculated according to RIS 61-2013.

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ИНДУКТИВТІ-БАЙЛАНЫСҚАН ПЛАЗМАМЕН АТОМДЫҚ-ЭМИССИЯЛЫҚ ӘДІСІМЕН МЫС ӨНДІРІСІНІҢ ҚАРА МЫС ҮЛГІЛЕРІНДЕ АСЫЛ МЕТАЛДАРДЫ (Au, Ag) АНЫҚТАУ

Аннотация. Бұл мақалада мыс өндірісінің қара мыс үлгілерінде алтын мен күмісті анықтау үшін индуктивті-байланысқан плазмамен атомдық-эмиссиялық әдістің зерттеу нәтижелері берілген. Әзірленген әдіс 28-56 г/т, күміс – 2000-3000 г/т диапазондарында алтынды анықтауға мүмкіндік береді. Дәлдікті бақылау талдаудың бақылау әдісі (сынамалы-гравиметриялық) және қоспалардың аттестацияланған мәндері бар мыс құрамының мемлекеттік стандартты үлгісін өлшеу арқылы жүргізілді. Әзірленген әдістеме өзінің метрологиялық сипаттамалары бойынша талдаудың бақылау әдісінен кем емес. Алтынға-242, 795 нм, күміске-328,068 нм үшін оңтайлы спектралды сызықтар таңдалды, олар өте сезімтал, спектралды кедергілері жоқ. РМГ 54-2002 сәйкес Ag, Au анықтау АЭС-ИСП градуирлеу сипаттамаларына статистикалық өңдеу жүргізілді, нәтижесінде орташа стандартты салыстырмалы ауытқулардың, a және b коэффициенттерінің стандартты ауытқуларының мәндері, ауытқулардың орташа квадраттарының қатынасы және бөлу квантилы алынды. РМГ 61-2013 сәйкес әзірленген әдістеменің дәлдігі, дұрыстығы, қайталануы, қайта орындалу көрсеткіштері есептелген.

Түйін сөздер: қара мыс, асыл металдар, балқыту, алтын, күміс, атомдық эмиссия, индуктивті-байланысқан плазма.

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АТОМНО-ЭМИССИОННЫЙ С ИНДУКТИВНО-СВЯЗАННОЙ ПЛАЗМОЙ МЕТОД ОПРЕДЕЛЕНИЯ БЛАГОРОДНЫХ МЕТАЛЛОВ (Au, Ag) В ОБРАЗЦАХ ЧЕРНОВОЙ МЕДИ МЕДНОГО ПРОИЗВОДСТВА

Аннотация: В данной статье представлены результаты исследования атомно-эмиссионного метода с индуктивно-связанной плазмой для определения золота и серебра в образцах черновой меди медного производства. Разработанный метод позволяет определять золото в диапазонах 28-56 г/т, серебро – 2000-3000 г/т. Контроль точности производился с помощью контрольного метода анализа (пробирно-гравиметрический) и с помощью измерения государственного стандартного образца состава меди с аттестованными

значениями примесей. Разработанная методика не уступает по своим метрологическим характеристикам контрольному методу анализа. Были подобраны оптимальные спектральные линии для золота – 242, 795 нм, серебра – 328,068 нм, которые обладают наибольшей чувствительностью, не имеют спектральных помех. Проведена статистическая обработка градуировочных характеристик АЭС-ИСП определения Ag, Au согласно РМГ 54-2002, в результате были получены значения средних стандартных относительных отклонений, стандартных отклонений коэффициентов a и b, отношение средних квадратов отклонений и квантиль распределения. Рассчитаны показатели точности, правильности, повторяемости, воспроизводимости разработанной методики согласно РМГ61-2013.

Ключевые слова: черновая медь, благородные металлы, плавление, золото, серебро, атомная эмиссия, индуктивно-связанная плазма.

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