Atomic-Emission Determination of Rhenium in Anthropogenic Raw Materials of Steel Production

Troeglazova A.V.[1*], Zlobina E.V.[1], Kudryavtseva G.S.[2], Kirillov A.D.[2], Karpov Y.A.[2]

[1] Department of Chemistry, al-Farabi Kazakh National University, Almaty, Kazakhstan
[2] «Giredmet» State Scientific-Research and Design Institute of Rare MetalIndustry, Moscow, Russia

Abstract

The method including microwave acidic dissolution of samples and atomic-emission analysis of rhenium for determination of rhenium in cupper-molybdenum and lead-cupper wares is proposed. The range of determination concentration of metal is 0.05 – 0.5 mass percent, standard deviation of repeatability is 0.002 – 0.01 %.

Introduction

Rhenium is a rare and trace element, which does not form its own minerals and, consequently, its deposits are absent. Therefore, rhenium is obtained as the associated metal during the processing of molybdenum ores and some types of anthropogenic raw materials. Due to the low rhenium content in the raw material its deficit is observed, despite the fact that rhenium is required for the production of heat-resistant alloys in aircraft and rocket engineering, catalysts, thermocouples [1-3]. This situation dictates the need for extraction of rhenium from the semi product of metal production and recycling. This, in turn, requires development of methods for determination of rhenium in various kinds of anthropogenic raw materials.

Atomic emission spectrometry with inductively coupled plasma (ICP-AES) is the most promising method for the determination of rhenium in the raw materials among the modern methods of analysis. The first stage in the implementation of this method is the dissolution of the sample. Rhenium-containing samples are recalcitrant. There are various methods of chemical sample preparation of rhenium-containing raw material samples described in the literature [4-7]. Sintering with oxides of calcium and magnesium, acid dissolution and alkaline fusion are used for the expansion of copper and molybdenum ores, minerals and concentrates. Matrix elements obtained after leaching the cake remain in the insoluble residue, and the elements passed into the solution do not affect the atomic-emission determination of rhenium. During sintering with calcium oxide solution after leaching has a higher alkaline reaction of the medium than during the sintering of magnesium oxide. In addition, the analytical lines of rhenium and calcium overlap each other during atomic-emission determination. So, magnesium oxide is basically used as a reagent for the sintering.

Alkaline fusion with the addition of oxidants is the method that ensures complete transferring the rhenium into the solution. However, the salt content is often too high in the solution obtained, which complicates the subsequent determination of rhenium by ICP-AES.

Dissolution of the mineral acids and mixtures thereof is the most effective and the fastest method of expansion. However, the formation of volatile oxide of rhenium (VII) by heating often leads to an underestimation of the analytical results. The obtained solutions have complex salt background and influence on atomic-emission determination of rhenium.

Most of these methods of decomposition are laborious and time consuming. Therefore, different physical effects are used to intensify them: acoustic and magnetic fields, the temperature increase by carrying out the process in a closed system. Various

---

*corresponding author. Email: troeglasovaa@mail.ru methods of expansion the samples of different nature under microwave heating are described in the literature [8-10].

The aim of this work is to develop the methods for determining rhenium in the secondary anthropogenic raw materials, including expansion of samples in the analytical autoclaves with subsequent determination of rhenium by ICP-AES.

Experimental

Samples were pre-milled, dried at 105°C to constant weight in Thermo SCIENTIFIC (USA) convection oven. Semi-quantitative analysis of samples was carried out using ARL OPTIM'X X-ray fluorescence spectrometer (Thermo Fisher Scientifics).

MKP-05 set of autoclave sample preparation with resistive heating, equipped with AP-3C analytical autoclaves [9], and MARS-5 microwave system (CEM, USA), equipped with HP-500 vessels for the decomposition of samples were used for the decomposition of samples of rhenium-containing raw materials in a closed system.

Rhenium content in solutions obtained after expansion was determined using Jobin Yvon 38R atomic-emission plasma spectrometer (France). The most sensitive line of rhenium of 227.5 nm which is free from overlaps of accompanying elements was selected experimentally for analysis. Conditions of the analysis are presented in Table 1.

Table 1

Operating conditions of atomic-emission determination of rhenium

Power of plasma	1000 W
Cooling flow of argon	13 L/min
Auxiliary argon flow	0.9 L/min
Spray flow of argon	0.93 L/min
Time of taking the sample into the plasma	60 s
Signal integration time	10 s

A standard solution containing 1000 μg/mL of Re was used for studies. Solutions of lower concentrations were obtained by diluting the aliquot parts of the standard solution. Measurement of analytical signal in all cases was carried out with respect to 1 M hydrochloric acid solution (background). Control the correctness of the analysis of series of samples was performed by varying the portions.

Three intermediates of copper-molybdenum and lead-copper production were investigated in this work: waste of molybdenum production (S-1), intermediate of molybdenum production (S-2) and leaden cakes (S-3). The results of semi-quantitative analysis of the samples are presented in Table 2.

Table 2

Chemical composition of rhenium-containing samples

Sample code	Sample name	Fraction of Re, %	Chemical composition, %		
S-1	Waste of molybdenum production	0.46	Mo=74.1 S=18.4 Fe=2.9	Se=1.2 Cu=0.4 Zn=0.3	Pb=0.6 As=0.2
S-2	Intermediate of molybdenum production	0.10	Mo=34.2 Fe=3.3	Cu=1.0 Pb=0.2	
S-3	Leaden cakes	0.05	Cu>1; Pb>10 Mo = 0.002 Mn = 0.005 Ag > 0.01 Zn = 0.15 Ni = 0.004	Cr = 0.005 Ti = 0.08 As = 0.01 Sb = 0.004 Bi = 0.15 B < 0.01	Ta < 0.01 CaO = 0.2 MgO = 0.2 Fe_2O_3 = 0.5 Al_2O_3 = 0.2 SiO_2 = 5

Four measurements of the analytical line intensity were performed for each solution obtained after decomposition of the sample, and then the average value was calculated. The mass concentration of rhenium (μg/mL) was found by average value, using the calibration characteristic. The average of *n*-parallel determinations, each of which is made from a single sample was taken as the test result ($\overline{C}$).

Completeness of transferring rhenium into the solution during autoclave expansion was controlled by comparing the results with the results of the analysis of rhenium after the decomposition of the samples in an open system (dissolving in nitric acid solution, alkali fusion with sodium peroxide, sintering with magnesium and calcium oxides). It was established that the expansion in the open system allows fully transferring rhenium into the solution, but does not ensure the complete dissolution of the sample (Table 2). Additional alkaline fusion of the residue after dissolving the sample in acids was carried out for controlling the completeness of decomposition of the samples.

The exposure time in the autoclave was varied to select the autoclave expansion conditions. Weight of sample was 0.1-0.2 g. The solution of nitric acid (1:2) was used as the reagent. During exposition for 15 and 30 minutes the temperature was maintained at 200°C, and for 1 and 2 h – 220°C. Optimal conditions of autoclave acid dissolution of samples correspond to the temperature of 200°C, holding time in the autoclave – 30 minutes (Figure 1). The selected parameters provide results comparable with the results of the analysis of solutions obtained after the decomposition by classical methods (Table 2), so further increases in temperature and increase the holding time in the autoclave are inappropriate.

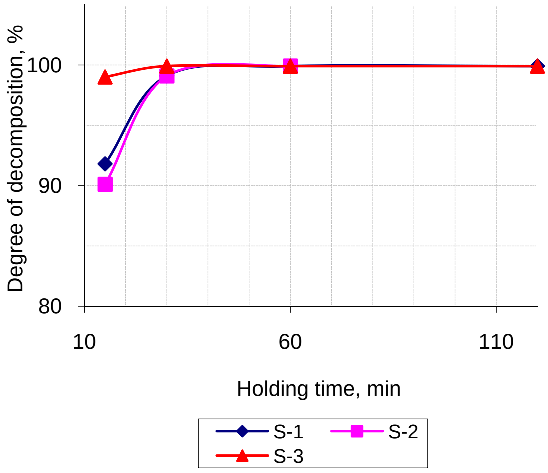

Fig. 1. Degree of decomposition of the samples from the time of exposure in an autoclave

Acid dissolving in the open and closed systems, alkali fusion and sintering with magnesium and calcium oxides are tested to select the optimal method of decomposition the samples of different nature. n decompositions of samples taken from different batches were carried out for each method of sample preparation. The standard deviation, calculated from the average measurements for all the results of determinations (s) was used to estimate the random component of error.

Table 3

Results of the analysis of rhenium-containing samples (n - number of samples, $\overline{C}$ - the arithmetic mean of the results of analysis, s – standard deviation of repeatability)

Method of decomposition	Sample code	n	$\overline{C}$, % масс.	s,% wt.
Sintering with CaO	S-1	3	0.460	0.035
	S-2	3	0.092	0.009
Alkali fusion	S-3	3	0.056	0.001
Sintering with MgO	S-3	3	0.055	0.011
Acid dissolving in the open system	S-1	4	0.505	0.020
	S-2	4	0.102	0.004
	S-3	4	0.049	0.006
Acid dissolving in the closed system	S-1	8	0.495	0.009
	S-2	8	0.105	0.004
	S-3	8	0.057	0.002

Dissolving the samples in nitric acid (1:2) under microwave heating allowed:

- fully transferring rhenium into the solution and dissolve the inorganic matrix;
- to reduce the duration of the decomposition;
- to reduce the amount of reagents used and thus reduce the salt background of the solution.

Comparative data on the duration of decomposition and consumption of reagents per sample are shown in Table 4.

Table 4
Conditions of the decomposition of rhenium-containing samples

Method of decomposition	Decomposition duration, h	Reagent amount
Acid dissolving in the open system	1.5-2	30 mL of HNO_3 (1:2)
Alkali fusion	1	2-3 g of NaOH + 0.1 g of Na_2O_2
Sintering with MgO	1	Twofold excess of MgO relative to the mass of the sample
Sintering with CaO	4.5-5	Threefold excess of CaO relative to the mass of the sample + 0.1-0.2 g of $KMnO_4$
Acid dissolving in the closed system	0.7	10 mL of HNO_3 (1:2)

The technique of atomic-emission determination of rhenium in the intermediate of copper-molybdenum and lead-copper productions in the concentration range from 0.05 to 0.5% by mass was developed basing on these results. Assessment of the metrological parameters of methods was carried out in concordance with the requirements of ISO 5725:1994 [11]. Assessing the uncertainty in measurements was carried out according to guidelines of EURACHEM/CITAC [12]. Error and uncertainty of the analysis technique for various mass fraction of rhenium are presented in Table 5.

Table 5
Metrological characteristics of the technique of analysis of rhenium-containing samples
(n - number of measurements, n = 20; $\overline{C}$ - the arithmetic mean of the results of analysis, % wt.,
s - standard deviation of repeatability, s_R - standard deviation of reproducibility, P = 0.95,
u_c - the total standard uncertainty, U - expanded uncertainty)

Sample code	The results of analysis	Error, % wt.		Uncertainty, % wt.	
	$\overline{C}$, % wt.	s	s_R	u_c	U
S-1	0.495	0.009	0.014	0.012	0.024
S-2	0.105	0.004	0.006	0.004	0.008
S-3	0.057	0.002	0.003	0.002	0.004

Thus, the decomposition of samples of intermediates of copper-molybdenum and lead-copper productions is obtained by dissolving in nitric acid (1:2) at 200°C for 30 min in the analytical autoclaves with microwave heating. Describing method is proposed as an alternative to the laborious and lengthy decomposition in the open system. This method allowed achieving complete decomposition of the samples, reducing the duration of sample preparation, eliminating losses of volatile components and reducing the correction of the blank experiment by reducing the amount of reagents used. The technique of atomic-emission determination of rhenium in the intermediates of copper-molybdenum and lead-copper productions was developed on the basis of these studies. Standard deviation of the repeatability (s) of the results of analysis by developed technique is within 0.002-0.01% wt. at rhenium content in the range of 0.05% - 0.5% wt.

References

1. Palant A.A., Troshkina I.D., Chekmarev A.M. Metallurgy of rhenium. Moscow: Nauka, 2007, 298 p.
2. Borisova L.V., Ermakov A.N. Analytical chemistry of rhenium. Moscow: Nauka, 1974, 321 p.
3. Naumov A.V. Rhythms of rhenium (review of world market) // Proceedings of the universities. Non-ferrous metallurgy. 2007. – № 6. – P. 36-41.
4. Karpov Y.A., Savostin A.P. Methods of sampling and sample preparation. Moscow: BINOM. Knowledge Lab, 2003. – 243 p.

5. Vasilyeva L.N., Karpov Y.A., Shiryaeva O.A. Modern methods for determination of rhenium // Non-ferrous metals, 1991. - №7. - P. 44-49.
6. Borisova L.V., Fabelinskiyi Y.I., Plastinina E.I., Prasolova O.D. Extraction-atomic emission with inductively coupled plasma method for determination of trace amounts of rhenium in copper sulfide samples // Factory laboratory, 1990. - №12. – P. 10-12.
7. Ryazanova L.N., Shiryaeva O.A., Nikitenko M.O. Determination of rhenium in copper ores and products of their concentration by atomic-emission method with induction plasma // Factory laboratory,1990. - №12. – P. 8-10.
8. Kubrakova I.V. Microwave radiation in analytical chemistry: opportunities and prospects of using // Advances in the Chemistry. 2002. - № 4 (71). – P. 327-339.
9. Karpov Y.A., Orlova V.A. Modern methods of autoclave sample preparation in chemical analysis of substances and materials // Factory laboratory. Diagnosis of materials, 2007. – V.73 – № 1 – P. 4-11.
10. V. Camel. Trends in Anal. Chem., V. 19, № 4, P. 229 (2000)
11. ISO 5725:1994. Accuracy (trueness and precision) of measurement results, Part 1-6: Basic method for repeatability and reproducibility of a standard measurement method, ISO, Case postale 56, CH-1211, Genève 20, Switzerland.
12. EURACHEM/CITAC Guide Quantifying Uncertainty in Analytical Measurements. Second Edition. 2000.

Received 9 December 2010