Determination of Calibration Characteristics of X-Ray Fluorescent Analysis of Rhenium

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Abstract

Extraction concentration of rhenium by a melt of tetraoctylammonium bromide in paraffin was used with the aim of preparation of calibration samples for roentgen fluorescent analysis. The calibration characteristics of the roentgen fluorescent analysis of rhenium is established, its linearity is evaluated, a limit of detection and a limit of quantification (determination) of rhenium are calculated. The maximal value of the relative total standard uncertainty of the calibration characteristic does not exceed 1.45 %.

Introduction

The ultralow abundance of rhenium in the nature, growth of its consumption in the petrochemical industry and aerospace instrument production condition the scales of manufacture of rhenium and necessity of perfecting of the methods of its analysis in various objects [1, 2]. A variety of objects of the analysis (ore, concentrates, powder, candle ends, muds, slags, final tailings, scrubbing sulfuric acid, metallic rhenium, perrhenates, heat-resisting alloys, catalysts, etc.) and the wide interval of the rhenium content in these objects explain the abundance of existing methods of the analysis [3, 4].

The topical problem of the analytical control of technological process is testing of low concentration of rhenium at the level of less than 10^{-3}%. The combination of preliminary concentration and instrumental analysis of rhenium allows one to reduce a determination limit of metal. Extraction by reagents of various natures is widely used as a method of rhenium concentration. Use of easily fusible diluent (paraffin) allows one to get a firm homogeneous extract which is easily transformable into a sample-radiator. This sample must satisfy the requirements of the roentgen fluorescent analysis (RFA) such as uniform distribution of metal in volume of a sample and its stability in time. In this case the element composition of a matrix does not influence the intensity of an analytical signal of rhenium. Thus, the problem of availability of standard samples of rhenium-containing materials of varied nature is solved.

Traditionally the X-ray fluorescence analysis is used for testing high contents of various elements. However, preliminary 10-100 times concentration, and the simplicity of methods of preparation of samples-radiators for XRF expand opportunities of the method and allow to use it for the analysis of "poor" rhenium-containing samples. The important tool to ensure the reliability and accuracy of the obtained results is the determination of calibration characteristic (CC) of X-ray fluorescence spectrometer.

The aim of the present work consists of determination of calibration characteristic of X-ray fluorescence analysis of rhenium and estimation of its metrological parameters.

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Experimental

The standard solution of rhenium (SSS № 100043-2) was used for the purposes of investigation. Working solutions of rhenium of smaller concentration were prepared by consecutive dilution of the initial solution. The necessary acidity (pH=1.5-2.0) in solutions was established using the 0.1M solution of H_2SO_4. The pH of solutions was controlled using ionomer I-160 MI.

Tetraoctylammonium bromide (TOAB) was used as an extraction reagent, paraffin was used as a thinner. The 20% of highest alcohols (HA) of fraction C_{17}-C_{20} was injected into extractant with the function of the modifier for improvement of the division of phases. The liquid extraction by the melt of extractant (0.15 M TOAB-HA-paraffin) was carried out in accordance with the following conditions: the ratio of organic and water phases V_O:V_L=1:10; the contact time of phases - 3 minutes; temperature – 70-80°C. After the extraction the phases were separated and analyzed for the contents of rhenium. The solid extract was transformed into a radiating sample for X-ray fluorescence analysis (RFA). The signal intensity of an analytic line of rhenium in the sample-radiator was determined using the scanning vacuum roentgen fluorescent spectrometer "Spectroscan MAKS-GV" ("Spectron", Russia). In the water phase the residual contents of rhenium after extraction was determined using the ICP mass spectrometer "Agilent-7500" (Agilent Technologies, Japan).

Results

For a determination of calibration characteristics 7 calibration samples (CS) with the known contents of rhenium were used. The range of concentration of metal in samples-radiators was $1.27 \cdot 10^{-4}$ - $3.26 \cdot 10^{-3}$ %.

Calibration samples were prepared using the following methods. The sample of extractant TOAB-HA-paraffin and a solution of rhenium (VII) (pH = 1.5-2.0) were introduced into the extraction vessel. A mix was heated up to a melting point of extractant. A vessel had been shaken manually for 3 minutes. After the extraction a mix was cooled up to room temperature and a solid extract was separated. The obtained extract was transformed into samples-radiators for RFA. The extract was melted and introduced into the metal cell of the predefined size and form. The prepared samples were solid, compact, homogeneous and having a smooth surface.

The preliminary stage of rhenium analysis using X-ray fluorescence spectrometer is the choice of the modes of measurements of an analytical signal. For this the qualitative analysis of prepared calibration samples was carried out with the maximal and minimal contents of rhenium with the minimal exposition (0 seconds) obtaining a spectrum in the whole operating range of the equipment. The analysis on separate sections was carried out according to reference values of the wavelengths increasing an exposition. It is established that the samples do not contain the elements capable to influence the analytical signal of rhenium. The modes of measurements of CS for an establishment of calibration characteristics are shown in table 1.

Table 1

Parameters of measurement of calibration samples

Crystal-analyser	LiF200
Current density	1 мA
Time of exposure (dependence on the range of concentration of rhenium in CS)	30-50 seconds
Analytical line	Re Lα1, order 1
Wave length	1437,0 мÅ
Accounting of the drift	Fe Kβ1, order 1
Accounting of background	On two points

The measurement of intensity of an analytical signal (quantity of pulses per second) was carried out for each sample 6 times. The contents of rhenium in CS and the average values of intensity corresponding to them are shown in table 2. Using the obtained values, the graphs of the calibration characteristic were constructed which describe the dependence of intensity of an analytical signal of rhenium on the contents of metal in CS (%) (fig 1).

The correlation coefficient of calibration characteristics shown in figure 1 is 0.9999, which evidences the strong correlation between the values of x (the rhenium contents) and y (signal intensity) [5].

The calibration characteristic was processed according to ISO 11095 [6] and RIS 54-2002 [7]. For the construction of linear calibration function the following statistical regression model is used:

$$y_n = a + bx_n \qquad (1)$$

where $\overline{y}_n$ – average value of intensity (pps), n = 1, 2, …, N; x_n - the contents of rhenium in CS, %; a, b – model parameters.

Table 2

The RFA measurements results (n - number of CS, C_{Re} - the content of rhenium in CS, %; $\bar{I}_n$ - average value of intensity, pps)

n	1	2	3	4	5	6	7
C_{Re}, %	0	$1.27{\cdot}10^{-4}$	$4.32{\cdot}10^{-4}$	$1.11{\cdot}10^{-3}$	$1.93{\cdot}10^{-3}$	$2.82{\cdot}10^{-3}$	$3.26{\cdot}10^{-3}$
$\bar{I}_n$, pps	2560	2873	3610	5245	7230	9470	10550

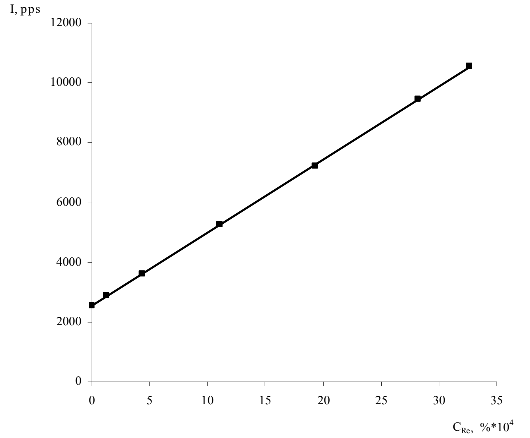

Fig. 1. The intensity of an analytical signal of rhenium dependence on the contents of metal in CS

The coefficient *a* corresponds to the value of a blank experiment, the regression coefficient *b* is a measure of sensitivity of the method of analysis (sensitivity coefficient). The choice of the method of estimation of coefficients *a* and *b* in the equation (1) is determined by a ratio of the deviation of x_n and $\bar{y}_n$ values which was calculated using formulas (2, 3) [6, 7].

$$\gamma_n = \frac{S_{x_n}\bar{y}_n}{S_{\bar{y}_n}x_n}, \tag{2}$$

where y_n – the ratio of the relative standard deviations; S_{x_n} – a standard deviations of values x_n; $S_{\bar{y}_n}$ – a standard deviation of values $\bar{y}_n$ in a point *n*.

Then the average value of relative standard deviations *y* was calculated using the following formula

$$\bar{\gamma} = \frac{1}{N}\sum_{n=1}^{N}\gamma_n\ , \tag{3}$$

Because the arithmetical mean value of relative standard deviations is $\gamma \leq 0.4$, the calibration characteristic was determined using a least-squares method (table 3).

The check of adequacy of mathematical model reduces to the check of linearity of calibration characteristics by Fisher's test (4) [6, 7].

$$V_y = \frac{N(J-1)Q_{y_1}}{(N-2)Q_{y_0}} \tag{4}$$

where V_y – the ratio of average squares of deviations (P = 0.95), Q_{y0} – the weighed total of squares of deviations y_{nj} (*j* – number of parallel measurements of CS, *j*=1, …, J) from average values of $\bar{y}_n$; Q_{y1} – the weighed total of squares of deviation of calculated values $\hat{y}_n$ from average values $\bar{y}_n$).

The obtained value V_y (table 3) were compared to tabular value of quantile of F-distribution with degrees of freedom $V_1 = N - 2$ and $V_2 = N(J - 1)$. Because of $V_y < F(V_1, V_2)$ the calibration characteristic is linear in a range of concentration of $1.27{\cdot}10^{-4}$ % - $3.26{\cdot}10^{-3}$ % at confidence probability of 0.95.

Table 3

The results of statistical analysis of CC (S_a and S_b – a standard deviations of factors *a* and *b*; $F(V_1, V_2)$ – a tabular value of Fisher's test with the number of degrees of freedom $V_1 = N - 2$ and $V_2 = N(J - 1)$., *J* – a number of parallel measurements of *n* CS)

γ	*a*	S_a	*b*	S_b	V_y	$F(V_1, V_2)$
0.01	$2.52{\cdot}10^{3}$	36.50	$2.46{\cdot}10^{6}$	$1.39{\cdot}10^{4}$	2.40	2.49

A series of analyses of a background sample were carried out, its average value and a standard deviation were calculated to find the limit of detection [8]. The limit of detection of rhenium C_{minP} calculated using the formula (5) is equal $9.75\cdot10^{-5}$ %.

$$C_{\min P}=\frac{3S_y}{S} \tag{5}$$

Where S_y – a standard deviation of a background analytical signal (blank experiment); S – a sensitivity coefficient.

For finding the lower limit of determined contents the relative standard deviations of concentrations $S_r\,(c)$ from the contents c [8] were calculated according to the formula (table 4) (6):

$$S_r(c)=\frac{S(I)}{Sc}, \tag{6}$$

where $S_r(c)$ – a relative standard deviation of concentration; $S(I)$ – a standard deviation of intensity; S – a sensitivity coefficient; c – the rhenium contents, %.

Table 4

Calculation of the limit of determination of rhenium

C_{Re}, %	$1.27\cdot10^{-4}$	$4.32\cdot10^{-4}$	$1.11\cdot10^{-3}$	$1.93\cdot10^{-3}$	$2.82\cdot10^{-3}$	$3.26\cdot10^{-3}$
$S(I)$	24.28	13.31	7.90	6.95	9.80	4.13
$S_r(c)$	$7.38\cdot10^{-2}$	$1.19\cdot10^{-2}$	$2.75\cdot10^{-3}$	$1.39\cdot10^{-3}$	$1.34\cdot10^{-3}$	$4.89\cdot10^{-4}$

The limit of quantification – $1.27\cdot10^{-4}$ % corresponds to such minimal concentration of rhenium which can be determined with a relative standard deviation of $S_r \le 0{,}33$.

The estimation of uncertainty of calibration of samples was carried out according to manual EURACHEM/CITAC [9].

During the calculation of uncertainty of preparation of calibration samples it is important to reveal the sources of uncertainty which in this case are: uncertainty of preparation of transfer solutions B and C, volume of the pipette and flask (Table 5).

Table 5

Values of uncertainty of the factors influencing the uncertainty of preparation CS

№	№ CS	Name of uncertainty source	Value x	Standard uncertainty u(x)	Relative standard uncertainty u(x)/x
1	4-7	Coefficient of dilution of transfer solution A (for transfer solution B)	10	0.098	0.0098
	2-3	Coefficient of dilution of transfer solution B (for transfer solution C)	10	0.1387	0.01387
2	1-7	Pipette volume	10.0	0.0413	0.00413
3	1-7	Flask volume	50.0	0.0523	0.001046

The contribution of uncertainty relating to preparation of transfer solutions B and C is the largest. The values of standard uncertainty of CS were calculated using the formula (7) (table 6):

$$u_c(C_{\mathrm{Re}})=C_{Re}\cdot\sqrt{(\frac{u(\tilde{o})_1}{\tilde{o}_1})^2+(\frac{u(\tilde{o})_2}{\tilde{o}_2})^2+(\frac{u(\tilde{o})_3}{\tilde{o}_3})^2} \tag{7}$$

where $u_c(C_{\mathrm{Re}})$ – a standard uncertainty of calibration samples.

The relative standard uncertainty of preparation of calibration samples was calculated using the formula (8):

$$u_c(C_{\mathrm{Re}})_{rel}=\frac{u_c(C_{\mathrm{Re}})}{C_{\mathrm{Re}}}\cdot100 \tag{8}$$

$u_c(C_{\mathrm{Re}})_{rel}$ – the relative standard uncertainty of CS.

Table 6

Results of calculation of uncertainty of calibration graph

№	C_{Re}, %	Standard uncertainty of CS u_c, %	Relative standard uncertainty Of CS $u_c(C_{\mathrm{Re}})_{rel}$, %
1	0	0	0
2	$1.27 \cdot 10^{-4}$	$1.84 \cdot 10^{-6}$	1.45
3	$4.32 \cdot 10^{-4}$	$6.27 \cdot 10^{-6}$	1.45
4	$1.11 \cdot 10^{-3}$	$1.19 \cdot 10^{-5}$	1.07
5	$1.93 \cdot 10^{-3}$	$2.06 \cdot 10^{-5}$	1.07
6	$2.82 \cdot 10^{-3}$	$3.01 \cdot 10^{-5}$	1.07
7	$3.26 \cdot 10^{-3}$	$3.48 \cdot 10^{-5}$	1.07

Under the increase of rhenium concentration the decrease of uncertainty of preparation of calibration samples is observed and the maximum value of standard uncertainty is 1.45 %.

Conclusions

The preparation of calibration samples for X-ray fluorescence analysis of rhenium was carried out using the extracts obtained after the extraction of rhenium by melt TOAB-HA-paraffin. The used extractant which is the matrix of a sample-radiator for RFA did not influence the intensity of an analytical signal of rhenium.

The experimental data obtained for CS are used for plotting calibration characteristics of X-ray fluorescence analysis of rhenium. The correlation coefficient of determined calibration characteristics was 0.9999. The estimation of regression coefficient of the chosen mathematical model was carried out using a least-squares method. The calibration characteristic is linear in the range of rhenium contents of $1.27 \cdot 10^{-4}$ % - $3.26 \cdot 10^{-3}$ % with confidence probability 0.95. The limit of detection and the limit of definition of rhenium were calculated and are equal $9.75 \cdot 10^{-5}$ % and $1.27 \cdot 10^{-4}$ % correspondingly.

The combination of extraction concentration and X-ray fluorescence analysis of rhenium directly in the extracts enables the determination of the metal at a level of $n \cdot 10^{-4}$ % with the relative standard uncertainty which does not exceed 1.45 %.

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