

# Extraction of rhenium (VII) by tetraoctylammonium bromide mixed with low-melting thinners

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## Abstract

Regularities of extraction of rhenium (VII) melt tetraoctylammonium bromide in a mixture of higher alcohols and paraffin were determined. Quantitative extraction of measurements obtained in the range of pH of the aqueous phase 1.5–2.0 was carried out. It was shown that the degree of extraction of rhenium is reduced during the transition from sulfuric to nitric acid. The introduction of extracting 20% of higher alcohols improved the solubility of the extracted complex in paraffin. The composition of the complex, calculated, was  $3.37 \pm 0.4$ .

**Keywords:** bromide tetraoctylammonium; extraction; higher alcohols; paraffin; rhenium.

## Introduction

Low concentration of rhenium in natural and industrial sites necessitates its concentration. The most widespread method is liquid extraction. Similar to aqueous solutions, rhenium in a wide range of acidity of the aqueous phase is in the form of stable perrhenate ion (Borisova and Ermakov 1974); neutral and anion-exchange extractants are used for its extraction.

Effective extractants for rhenium are neutral organophosphorus compounds, di(izo)(octyl)methylphosphonate (Travkin et al. 1975, Adamova and Ponomareva 1980, Chekmarev et al. 1999, Palant et al. 2007), tri-*n*-butylphosphate (TBP) (Travkin et al. 1975, Adamova and Ponomareva 1980, Chekmarev et al. 1999, Palant et al. 2007), their derivatives hexabutyltriamide of phosphoric acid, alkyl phosphine sulfides (Travkin et al. 2003a,b), synergistic mixtures of TBP with trioctylphosphine oxide or di-2-ethylhexilphosphoric acid (Palant et al. 2007), and oxygen-containing reagents (alcohols, ketones) (Borisova and Ermakov 1974, Chekmarev et al. 1999, Palant et al. 2007, Kassikov and Petrova 2009). To

increase the solubility of the extraction reagents and extracted compounds in the solvents, up to 25% vol. of higher alcohols is added to the extractants.

Among the anion-exchange extractants, salts of secondary and tertiary amines are most commonly used. Among them, the most common are tri-*n*-octylamine (TOA) and its technical analog trialkylamine C<sub>7</sub>–C<sub>9</sub>, which extract rhenium from solutions in a wide range of acidity. Extraction of rhenium by TOA depends on the nature and concentration of mineral acid and decreases in the series H<sub>2</sub>SO<sub>4</sub> > HCl > HNO<sub>3</sub>. The decrease in the degree of extraction from sulfuric acid to nitric acid is caused by the competing extracting action of the acid itself (Palant et al. 1973).

Quantitative extraction of rhenium without addition of higher alcohols as a modifier can be achieved in the extraction of metal by di(izo)dodecylamine (DIDA) which is a secondary amine. The effectiveness of DIDA is explained by steric advantages over tertiary amines and less competitive ability of a mineral acid (Chekmarev et al. 1999, Palant et al. 2007).

Salts of quaternary ammonium bases (QAB) are the extractants which are capable of extracting rhenium from acidic, neutral and alkaline media. Extraction of rhenium by the salts of QAB is carried out in alkaline medium to separate rhenium from molybdenum. However, re-extraction of rhenium from the organic phase containing QAB is difficult and involves the use of harsh chemicals (chlorine or nitric acid, ammonium thiocyanate) (Palant et al. 2007).

Extraction methods for concentration and extraction which are widely used in the technology of rhenium production have been used successfully on the stage of sample preparation in determination of low concentrations of rhenium in various natural and industrial sites. Combined techniques described in the literature involve determination of rhenium by different methods in the aqueous phase after its re-extraction (Borisova and Ermakov 1974, Travkin et al. 1975, Chekmarev et al. 1999, Palant et al. 2007). However, analysis is labor- and time-consuming owing to duration of separation of organic and aqueous phases and an additional stage of re-extraction.

These disadvantages can be eliminated by direct determination of rhenium in the organic extracts by the X-ray fluorescence method. Because X-ray fluorescence analysis (XFA) has specific requirements to the sample emitter, an important step in the development of combined techniques is the choice of extractant and method of producing the sample emitter. Conditions of XFA are fulfilled by macromolecular hydrocarbons of the paraffin series which are solid under normal conditions; they easily pass into the melt at temperatures above 60°C which allows the liquid extraction of rhenium (Gladyshev et al. 1985). After cooling, solid extracts

are molded into sample emitters by simple form filling. The conditions of quantitative determination of rhenium are required for the practical application of extraction. The main parameters affecting the distribution of rhenium between the organic and aqueous phases are acidity of the aqueous phase, concentration of extractant and modifier in the organic phase and temperature.

The aim of this study was to examine the patterns of extraction of rhenium (VII) by the melt salts of QAB.

## Materials and methods

A standard solution of rhenium (VII) with concentration of 0.02 M prepared by dissolving accurately weighed ammonium perrhenate in distilled water was used in this study. Working solutions of lower concentrations were obtained by diluting the initial solution. Necessary acidity of the prepared solutions was adjusted using 0.1 M solution of  $H_2SO_4$ ,  $HNO_3$  and NaOH. The pH values of the solutions were controlled by using an ionomer I-160 MI (Measuring equipment, Belorussia).

Tetraoctylammonium bromide (TOAB) was used as an extraction reagent in all studies, and aviation kerosene and paraffin for laboratory purposes were used as diluents. Higher alcohols (HA) of  $C_{17}$ – $C_{20}$  fraction were added to the extractant as a modifier to improve the phase separation.

Extractant containing TOAB-HA-paraffin was prepared by addition of the calculated amounts of TOAB and HA to the melt wax at a temperature of 70–80°C, by obtaining the homogeneous melt and then cooled with constant stirring.

The technology of rhenium extraction by the solution of TOAB in kerosene was as follows: the exact volume of extractant and the solution of perrhenate ion with a given value of the acidity of the aqueous phase were placed in a separating funnel with the capacity of 100 ml. The mixture was shaken for 3 min and aqueous phase was separated after complete phase separation. For the extraction of the metal by low-melting extractants, a sample of the extractant and the exact volume of the solution of perrhenate ion with a given value of the acidity of the aqueous phase were placed in an extraction vessel. After melting of the extractant (70–80°C), the mixture was shaken manually for 3 min. After cooling to room temperature, the solid extract was separated.

After phase separation the equilibrium pH and the residual content of rhenium in the aqueous phase were determined. Ratio of organic and aqueous phases was 1:10. Residual content of rhenium in the aqueous phase was determined by inductively coupled plasma mass spectrometry using the Agilent-7500 instrument (Agilent Technologies, Japan). Calibration was carried out by using the standard solution of rhenium prepared using SSS No 100043-2. Concentration of rhenium in the organic phase was calculated from the difference between metal concentrations in solution before and after extraction.

Studies on the effect of temperature on extraction were performed in thermostatted vessels. Extraction of metal at temperatures of 20°C–60°C was carried out using 0.01 M solution

TOAB-kerosene, and at 70–90°C melt TOAB-HA-paraffin was used as extractant.

## Results and discussion

Results of studies on the extraction of rhenium by TOAB-HA-kerosene solution with the concentration of TOAB of  $1 \times 10^{-2}$  M showed that quantitative extraction of metal is achieved at pH of 1.5 for 3 min of phase contact. The possibility of replacing the diluent kerosene with its chemical analog paraffin was studied.

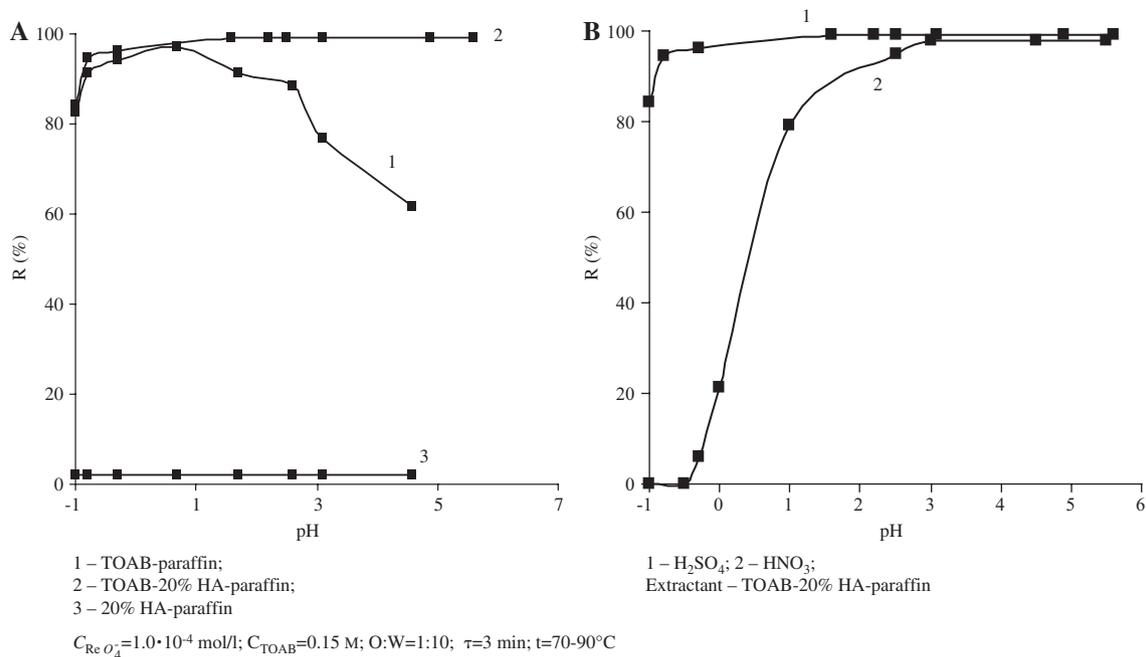
The degree of extraction of rhenium (VII) on the acidity of the aqueous phase in extraction of metal by the melts HA-paraffin-wax, TOAB-paraffin and TOAB-HA-paraffin are shown in Figure 1A. Higher alcohols do not extract rhenium in the whole range of acidity of the aqueous phase. The degree of extraction of rhenium by the melt of TOAB-paraffin decreases at pH above 1.5, which is apparently due to deterioration of solubility of the extracted complex in the organic phase. Best results are achieved in the extraction of the metal by the melt of TOAB-HA-paraffin in the range of concentrations of sulfuric acid of 0.1–3 mol/l and pH 0.1–5.5.

The universal method of expansion of rhenium-containing samples is their dissolution in sulfuric and nitric acids which gives minimal loss of metal when heating. Therefore, the effect of concentration of  $H_2SO_4$  and  $HNO_3$  to extract rhenium by the melt of TOAB-HA-wax was studied (Figure 1B). It was found that the increase in the concentration of sulfuric acid  $>0.5$  mol/l reduces the extraction of rhenium. From nitric acid solutions rhenium is extracted quantitatively only at pH  $\geq 2.5$ . This is due to competitive extraction of nitric acid by the salts of QAB (Chekmarev et al. 1999, Palant et al. 2007). Further studies were carried out with sulfuric acid solutions in the pH range of 1.5–2.0, which is a range of quantitative extraction of rhenium by the melt of TOAB-HA-paraffin.

Higher alcohols are not extractants for rhenium, and their addition to the diluent can also lead to poor extraction and thus the contents of HA in the composition of the extractant should be minimal. The effect of the concentration of HA and TOAB on the extraction of rhenium at the optimal pH of the aqueous phase was studied. The results are shown in Table 1. It was found that the decrease in the extraction of rhenium is caused by the content of HA at  $>40\%$  of the weight of the extractant. Homogeneous extract for preparation of the sample emitter fulfilling the conditions of XFA was obtained by the content of HA of 20 wt.%.

It is known that an increase in temperature leads to improved extraction of rhenium by the solutions of salts of tertiary amines in kerosene (Chekmarev et al. 1999, Palant et al. 2007). The effect of temperature on the extraction of rhenium (VII) by the salt of QAB was investigated in this study. It was observed that changes in the temperature in the range of 20°C–90°C have no effect on the extraction of the metal.

To describe the mechanism of the extraction process and the calculation of the concentration constants, it was necessary to determine the composition of the extracted complex



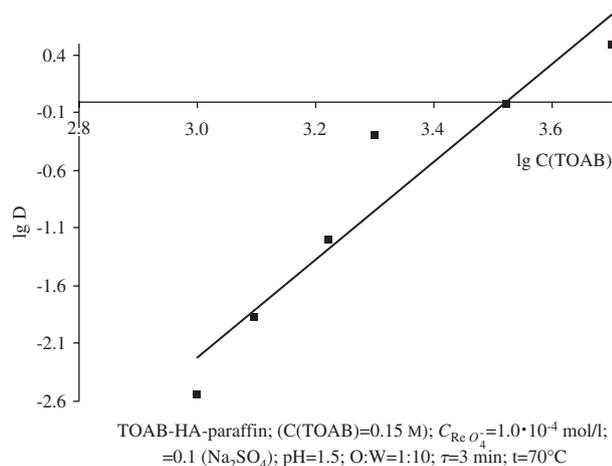
**Figure 1** Dependence of the degree of extraction of Re (VII) on the acidity of the aqueous phase.

**Table 1** The effect of concentration of higher alcohols (HA) on the extraction of rhenium (VII).

$\omega$ (HA), %	5	10	15	20	25	30	40	45	50	55
$R_{Re}$ , %	99.5	99.2	99.2	98.6	96.9	96.7	96.1	92.4	85.0	75.0

compound and, hence, the  $\text{ReO}_4^-$ :TOAB ratio. Determination of the solvate number was carried out using two independent methods; all experiments showed that ionic strength and temperature remained constant.

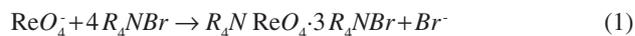
The equilibrium shift method was used to determine the Re-TOAB ratio. Distribution coefficients increased with increasing concentration of TOAB ( $R_4\text{NBr}$ ) (Figure 2). The slope ratio of the (distribution coefficients of rhenium-



**Figure 2** The logarithmic dependence of the distribution coefficients of Re (VII) on the concentration of TOAB in the organic phase.

TOAB concentration) logarithmic dependence is close to four; consequently, the solvate number is 4. Rhenium:TOAB ratio obtained by the isomolar series method is 1:4. Consequently, the organic phase extracted complexes of  $R_4\text{NReO}_4 \cdot 3R_4\text{NBr}$ .

Completed studies allowed the proposal of the extraction of rhenium by the melt of TOAB-HA-paraffin and calculation of the concentration constants of the extraction. The process proceeds by the anion-exchange mechanism. The extraction process method of rhenium by the melt of TOAB-HA-wax can be represented as:



with extraction constant of:

$$K_{ex} = \frac{[R_4\text{NReO}_4 \cdot 3R_4\text{NBr}] \cdot [\text{Br}^-]}{[\text{ReO}_4^-] \cdot [R_4\text{NBr}]^4} \quad (2)$$

Finding the logarithm of the expression, we obtain:

$$\lg K_{ex} = \lg D + \lg [\text{Br}^-] - 4 \lg [R_4\text{NBr}]$$

$$\lg K_{ex} \text{ is } 3.37 \pm 0.40. \quad (3)$$

## Conclusions

Thus, it was found that the extraction of rhenium by 0.15 M TOAB melt with BC-wax depends on the nature and concentration of mineral acid; the distribution coefficients of rhenium increase in passing from nitric to sulfuric acid. Reduction of metal extraction in strong acidic solutions is caused by the influence of the competitive extraction of mineral acids. Higher alcohols do not show extraction properties, their introduction

into the extractant leads to better dissolution of the extracted complex in the organic phase, but the content of HA in the composition of the extractant in excess of 40% leads to the decrease in extraction of rhenium. Changing the temperature in the range from 20°C to 90°C has no effect on the extraction of rhenium.

Using the equilibrium shift method and isomolar series method, the molar ratio of components in the extractable compound Re:TOAB is 1:4, which corresponds to the complex composition  $R_4NReO_4 \cdot 3R_4NBr$ , and  $\lg K_{ex}$  is  $3.37 \pm 0.4$ . Thus, the melt of 0.15 M TOAB in paraffin with 20% wt. addition of higher alcohols as a modifier can be recommended for extraction of rhenium (VII) from solutions at pH 1.5–2.0 and the ratio of organic and aqueous phases of 1:10. The obtained solid extracts can be used for analysis by the XFA method.

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