

COMPLEXATION OF RHENIUM WITH BENZHYDROXAMIC ACID IN HYDROCHLORIC ACID SOLUTIONS

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Abstract: It was disfigured by spectrophotometric method as a result of exposure to radiation (VII) with benzhydroxamic acid in an acidic medium in the presence of tin (II). The stability and composition of the complexes are determined. A spectrophotometric method for the determination of rhenium in the presence of a number of elements has been developed, used for the analysis of alloys and technological solutions obtained by firing molybdenum concentrates.

Keywords: rhenium, reagent, compound, composition, constant, component, density.

Benzhydroxamic acid (BHA) and its analogues are widely used in analytical chemistry. BHA forms colored compounds with metal ions Co^{2+} , Cu^{2+} , Ni^{2+} , Fe^{3+} , Cr^{3+} , Ti (IV) , U (VI) , Mo (VI) and others, extracted with ketones and alcohols [1-3].

We studied the complexation reaction of rhenium with BHA in hydrochloric acid solutions. The optimal conditions for interaction in the $\text{Re (VII)-HCl - BHA-Sn (II)}$ system, the composition and stability of the compounds were determined, and a spectrophotometric method for determining rhenium in the presence of accompanying elements was developed.

To prepare rhenium solutions, NH_4ReO_4 and KReO_4 salts, purified by recrystallization, were used. A hydrochloric acid solution of rhenium (V) in the form of K_2ReOCl_5 was prepared according to the procedure [2]. As a reagent for rhenium, we used ordinary grade BHA, purified by recrystallization from ethyl acetate.

Complexation of rhenium with BHA. When perrhenate ion interacts with BHA in HCl in the presence of a reducing agent, a greenish-yellow colored compound with λ_{max} 340-350 nm is formed. The optical density reaches a maximum at 3-4 M HCl. An increase or decrease in acid concentration reduces the optical density of solutions (Fig. 1), which is due to a change in the state of rhenium and the reagent or a shift in equilibrium towards the formation of chloride complexes.

Rhenium reacts with a valency <7 . Therefore, to shift the equilibrium towards the formation of low-valent rhenium, a large excess of the reducing agent Sn (II) is required.

To achieve the maximum optical density of solutions, a 100-fold excess of the reagent containing 1.2 g of tin (II) is required. Measurements showed that the reaction proceeds in 2.5-3.0 hours at 20-30 °C. The formation of a rhenium compound with BHA is influenced by the nature of the acids: in HCl, H_2SO_4 , H_3PO_4 and CH_3COOH , the optical density is highest in hydrochloric and sulfuric acid media. However, the reaction proceeds faster in a sulfuric acid environment due to heating of the solutions. A precipitate forms in phosphoric acid, making it difficult to determine rhenium. Determination is impossible in nitric and perchloric acids.

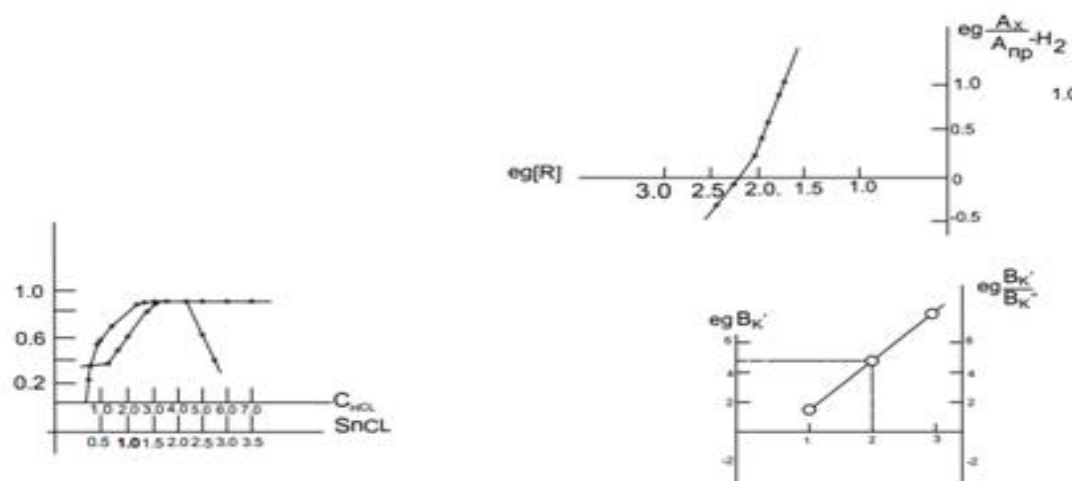
Composition and stability of the rhenium complex with BHA. Using the methods of equilibrium shift and intersection of curves (Fig. 2), the molar ratios of the reacting components were found at a constant concentration of rhenium ($2 \cdot 10^{-4}$ M), HCl (3.3 M), tin chloride and various concentrations of BHA at $\lambda_{\max} = 340-350$ nm .

In solutions, in addition to a compound with a molar ratio of Re:BHA = 1:2 at low concentrations of BHA ($2 \cdot 10^{-3}$ - $8 \cdot 10^{-3}$ M), there is a compound with a ratio of Re:BGA = 1:1.

The conditional instability constant of the complex, determined by the methods of equilibrium shift, by the saturation curve, as well as by the graphical method of intersection of curves (Figure 2) is equal to $2.58 \cdot 10^{-5}$; $1.81 \cdot 10^{-5}$.

The mechanism of interaction of rhenium with BHA. According to the analysis of absorption curves of the Re (VII) – HCl – BHA–Sn (II) system, the retention of shape, the position of the absorption maximum, as well as the formation under optimal conditions of one complex compound of composition 1:2 with $\lambda_{\max} = 340-350$ nm were established.

It has been determined that the interaction of Re (V), taken in the form of K_2ReOCl_5 in HCl, with BHA produces a compound whose absorption spectrum is identical to the spectrum of the compound obtained in 3.3 N HCl in the presence of tin (II). These results suggest that rhenium can be considered pentavalent in its complex with BHA.



Rice. 1. Influence of the concentration of HCl (1) and SnCl₂ (2) on the optical density of solutions of the rhenium complex with BHA ($C_{Re} = 2 \cdot 10^{-4}$ M; $S_{BHA} = 2 \cdot 10^{-4}$ M).

Rice. 2. The composition of the rhenium complex with benzhydroxamic acid, determined by the methods of equilibrium shift (1) and curve intersection (2) ($C_{Re} = 2 \cdot 10^{-4}$ M, 3.3 N HCl).

The sign of the charge of the complex group was determined by the ion exchange chromatographic method using ion exchangers of the AB-17 and KU-2 brands. Its anionic nature has been proven.

To confirm the composition data, a solid compound was isolated in which the ratio of Re and BHA, according to elemental analysis, was 1:2.

The IR spectrum of the compound isolated in solid form contains intense bands at 925 and 965 cm^{-1} , due to symmetric and antisymmetric vibrations of the ReO_2 group. In contrast to the IR spectra of BHA, a significant change occurs in the spectrum of the complex under study at 3310-3320 and 1630-1640 cm^{-1} , where the frequencies of stretching vibrations of the OH and CO groups are located, respectively. Thus, in the spectrum of the complex compound there is no stretching vibration band $\nu_{\text{C=O}}$, it decreases to 1620-1600 cm^{-1} .

Thus, complexation occurs due to the substitution of the proton of the OH group and the coordination of the carboxyl group to form a chelate ring.

Compliance with Beer's law in solutions of the complex. The absorption of the rhenium complex with BHA in 3.3 M HCl is proportional to the rhenium concentration in the range of 4-40 $\mu\text{g/ml}$. To construct a calibration curve, a certain amount of rhenium (up to 1000 μg) is placed in 25 ml flasks, 5 ml of a $1 \cdot 10^{-1}$ M solution of BHA, 6 ml of HCl (11.34 M), 6 ml of a 20% solution of SnCl_2 in HCl and add up to 25 ml of distilled water. After stirring, measure the optical density at $\lambda_{\text{max}} = 340\text{-}350$ nm in a cuvette with $l = 1$ cm after 3.0-3.5 hours.

The molar extinction coefficient calculated by the least squares method is 4540 ± 57 .

According to data on the influence of foreign elements on the determination of rhenium, 1000-fold amounts of Ca^{2+} do not interfere with the determination in hydrochloric acid solution; 500-fold – Ba^{2+} ; 400-fold – Mg^{2+} , Zn^{2+} , Ca^{2+} , Mn^{2+} ; 200-fold – Na^+ , K^+ , Pb^{2+} , Ni^{2+} , Fe^{3+} , Al^{3+} , Ga^{3+} , In^{3+} ; 100-fold – Sr^{2+} , W (VI); 50-fold – Cu^{2+} , Co^{2+} , V^{5+} ; 25-fold – V (V), Zr (IV); 10-fold – Tl^{3+} , Sb^{3+} , Ti (IV), Ge (IV); 5-fold – Os (IV); 2.5-fold – Nb^{5+} ; single - Cr (VI) and Mo (VI), also 200-fold amounts of bromine, tartrate, citrate ions and complexone III, 100-fold - iodide, phosphate, borate, acetate ions; 50-fold – oxalate ions and 10-fold – chlorate ions. Pd, Bi, Se, Pt interfere with the determination of rhenium (dark brown color).

Mo(VI) and W(VI) do not form complexes with BHA under optimal conditions, but are simultaneously reduced with rhenium by tin(II). Therefore, you should either increase the concentration of SnCl_2 or use masking reagents (tartaric or oxalic acid).

The good selectivity of the reaction of rhenium with BHA allowed us to develop a method for determining rhenium in alloys.

Determination of rhenium in alloys. Alloy TR-10 (0.1-0.2 g) was dissolved in concentrated hydrochloric acid under low heating. The cooled solution was then transferred to a 250 ml volumetric flask and diluted to the mark with water. To decompose alloys containing tungsten (VR-27), a sample (0.05-0.1 g) was placed in a conical flask, 20-30 ml of water and 5-10 ml of a 30% H_2O_2 solution were added and heated until it was completely dissolved. 1-2 ml of a 25% ammonia solution was added to the resulting solution and boiled for several minutes to destroy hydrogen peroxide. Then diluted to 150 ml and neutralized with 2-3 ml of concentrated HCl. The cooled solution was transferred to a 250 ml volumetric flask and diluted to the mark with water.

To determine rhenium, an aliquot of the solution (1-6 ml) was taken into a 25 ml flask, 6 ml (11.3 M) HCl, 5 ml of 0.1 M BHA solution, 1 ml of 5% tartaric acid (in the case of tungsten-rhenium alloy) and 6 ml of 20% SnCl_2 solution. After 3.5 hours, the optical density of the solution was measured in cuvettes with $l=1$ cm at $\lambda_{\text{max}}=340\text{-}350$ nm. The rhenium content was determined from the

calibration curve. We present the results of determining rhenium BGK in alloys TR-10 and VR-27 (samples TR-10-0.1532 g, VR-27-0.0903 n, n=5).

Сплав	Аттестованное содержание рения, г	Найдено рения, г		
		X	S	X ± σ
TR-10	0,01532	0,01529	0,0002236	0,01529 ± 0,00028
VR-27	0,02438	0,02470	0,001323	0,02470 ± 0,00164

The developed methods were introduced to control technological solutions obtained by roasting molybdenum concentrates containing rhenium, Mo, W, Re and residual sulfuric acid, as well as for the simultaneous and separate determination of rhenium and Mo using BHA.

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