Notes

Photometric Determination of Rhenium with Potassium Hexacyanoferrate(II) in Presence of Thiocyanate

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Potassium hexacyanoferrate(II)¹ has earlier been used as a complexing agent for rhenium in the presence of tin(II) chloride, forming a colored complex in hydrochloric acid solution. The method utilizing this reaction for the determination of rhenium, however, could not gain much importance for want of sensitivity; interferences from vanadium, tungsten, chromium, copper and platinum metals in particular also caused trouble. The intensity of the colored complex formed between lower valent rhenium, obtained on reduction with ascorbic acid, and potassium hexacyanoferrate(II) increases considerably in presence of thiocyanate with relatively higher tolerance limits of other ions on extraction into isopentyl alcohol. Therefore, the system presented below makes use of this fact to work out a determination procedure for rhenium. This involves the formation of a mixed ligand complex by the metal ion with hexacyanoferrate(II) and thiocyanate using ascorbic acid as the reductant.

Experimental

Reagents

Rhenium solution, 1 mg ml⁻¹. A stock solution of rhenium is prepared by dissolving 0.1554 g of potassium perrhenate, KReO₄ ("Specpure" Johnson Matthey & Co.) in distilled water containing a few drops of 5 M HCl which is finally diluted to 100 ml. Lower concentrations of rhenium at µg ml⁻¹ level are obtained by suitable dilutions therefrom.

Potassium thiocyanate. 20%.

Potassium hexacyanoferrate(II). A 2% solution of the reagent is prepared in distilled water afresh daily.

Ascorbic acid (Loba Chemie) is used as solid. Isopentyl alcohol (Qualigens) is distilled and the fraction distilling between 128–132°C is collected for use. Solutions of other metal ions (mg ml⁻¹) are prepared by dissolving their commonly available salts of chemically

pure grade in distilled water or diluted acid solutions.

For absorbance measurements, a UV-visible 140-02 spectrophotometer (Shimadzu, Japan) is used.

Synthetic and flue dust samples

Synthetic samples are prepared by mixing µg amounts of rhenium with suitable amounts of other, metal ions, as shown in Table 2.

A reverberatory flue dust sample from copper manufacture, containing no rhenium, is mixed with a solution of known content of rhenium and dried in an oven. After complete fusion of the sample with sodium peroxide in a nickel crucible, the leach is neutralized with conc. H₂SO₄ and made slightly alkaline with NaOH. It is boiled and the hydroxide precipitate is filtered and washed well with distilled water. The filtrate along with the washings is adjusted to the experimental conditions described below in the procedure for the determination of rhenium.

Procedure

To an aliquot containing 100 µgRe and/or other ions in a 25 ml beaker, add 500 mg ascorbic acid, 2.5 ml 10 M HCl, 4 ml 20% KSCN, 2 ml 2% potassium hexacyanoferrate(II) and dilute it to 10 ml. Gently mix the contents, heat gradually to 70°C and allow it to stand for 10 min at room temperature. The dark orange-yellow metal complex so formed is transferred to a 100 ml separatory funnel, diluted to 20 ml with water and extracted once with an equal volume of isopentyl alcohol for 1 min. The organic layer is filtered through a Whatman filter paper No. 41 to remove any suspended droplets of water, into a 25 ml volumetric flask, which is made up to the mark with the pure solvent. The absorbance of the complex is measured at 440 nm using a blank extract as the reference solution. Rhenium is determined from the calibration curve constructed from the data obtained in a similar manner by taking different amounts of the metal ion in each set and measuring their corresponding absorbance values.

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Fig. 1 Absorption spectrum of Re-complex in isopentyl alcohol. Curve A: 4 µgRe/ml measured against reagent blank; B: reagent blank measured against isopentyl alcohol.

Results and Discussion

Perrhenate ion, ReO_4^- , in the presence of thiocyanate, forms a dark orange-yellow complex with potassium hexacyanoferrate(II) on reduction with ascorbic acid in hydrochloric acid solution at a temperature of *ca.* 70°C. The absorption spectrum of the metal complex indicates that λ_{max} lies at 440 nm, where the absorbance of the reagent blank is minimal (Fig. 1).

At 2 M (mol dm⁻³) of hydrogen ion, the absorbance of the metal complex in different acid, solutions decreases in the order—HCl > H₂SO₄ > H₃PO₄ > CH₃COOH, if other aqueous conditions are kept the same in each case (*i.e.* Re=100 µg, ascorbic acid=500 mg, KSCN=4 ml, potassium hexacyanoferrate(II)=2 ml, temperature *ca.* 70°C, color development time=10 min). Hence, hydrochloric

acid provides a suitable medium for the system.

Various operative parameters affecting the absorbance of the metal complex, namely temperature, color development time, HCl concentration, ascorbic acid, thiocyanate and potassium hexacyanoferrate(II) are shown in Table 1. From these studies, we concluded that for 100 µg Re: 2.3–2.8 M HCl, 0.25–1.50 g of ascorbic acid, 3.8–4.2 ml KSCN, 1.8–4.0 ml potassium hexacyanoferrate(II) in 10 ml volume, heating to 67–73°C, 8–15 min color development time, dilution to 20 ml and shaking once for 1 min with an equal volume of isopentyl alcohol, are the optimum conditions for the quantitative transfer of the metal complex to the solvent phase. Its absorption is measured at 440 nm after making up the volume to 25 ml as described in the procedure.

Under the conditions chosen for the procedure, the extraction of the metal complex has also been tried in various solvents. The absorbance is found to decrease in the order—*isopentyl alcohol* > *isopentyl acetate* > *ethyl acetate* > *isopentyl alcohol-chloroform* (1:3) > *isobutyl methyl ketone* > *ethyl methyl ketone*. It is almost negligible in case of pure chloroform and benzene. Hence, *isopentyl alcohol* is considered to be a suitable extracting solvent for the metal complex.

Effect of diverse ions

Sulfate (200 mg), acetate (100 mg), citrate (50 mg), tartrate (50 mg), phosphate (100 mg) and EDTA (50 mg) do not affect the absorbance of the metal complex; but chloride (100 mg) and fluoride (50 mg) increase it slightly. The presence of oxalate (100 mg), nitrate (100 mg), thiourea, 50 mg, and H₂O₂, 1 ml 30%w/v, lowers the absorbance. The figure shown in brackets indicates the amount of the sodium salt of the anion

Table 1 Effect of various parameters on the absorbance of the Re-complex

Temperature ^a (°C)	40	45	50	55	60	65	67	70	73	75	80	85
Absorbance	0.025	0.040	0.115	0.210	0.590	0.610	0.620	0.620	0.620	0.615	0.590	0.575
Color development time ^b (min)	0	5	8	10	15							
Absorbance	0.460	0.605	0.620	0.620	0.620							
Ascorbic acid ^c (g)	0.00	0.05	0.10	0.20	0.25	0.50	1.00	1.50				
Absorbance	0.510	0.565	0.590	0.610	0.620	0.620	0.620	0.620				
HCl ^d [M]	0.0	0.5	1.0	1.5	2.0	2.3	2.5	2.8	3.0	3.5	4.0	
Absorbance	0.011	0.030	0.125	0.585	0.610	0.620	0.620	0.620	0.607	0.580	0.567	
KSCN ^e (ml)	0.0	0.5	1.0	2.0	3.0	3.5	3.8	4.0	4.2	4.5	5.0	6.0
Absorbance	0.010	0.210	0.364	0.575	0.589	0.615	0.620	0.620	0.620	0.610	0.592	0.565
Potassium hexacyanoferrate(II) ^f (ml)	0.0	0.5	1.0	1.5	1.8	2.0	2.5	3.0	4.0			
Absorbance	0.600	0.610	0.620	0.635	0.640	0.640	0.640	0.640	0.640			

[Conditions] a. Re=100 µg, ascorbic acid=500 mg, HCl=2.5 M, KSCN=4 ml, potassium hexacyanoferrate(II)=1 ml, color development time=10 min, temperature=variable. b. Temperature=70°C, other conditions being the same as in (a) except for variation in color development time. c. Color development time=10 min, other conditions being the same as in (b) except for variation in the amount of ascorbic acid. d. Ascorbic acid=500 mg, other conditions being the same as in (c) except for variation in acid concentration. e. HCl=2.5 M, other conditions being the same as in (d) except for variation in KSCN concentration. f. KSCN=4 ml, other conditions being the same as in (e) except for variation in potassium hexacyanoferrate(II) concentration.

Fig. 2 Ringbom plot of Re-complex at 440 nm.

added initially to the aqueous solution.

The cations which do not show any absorption under conditions of the procedure include Ca^{II} , Ba^{II} , Mg^{II} , Hg^{II} , Bi^{III} , Ce^{IV} , As^V , 5 mg/20 ml; Ag^I , Mn^{II} , Zn^{II} , Pb^{II} , Sb^{III} , Al^{III} , 2.5 mg/25 ml; Cu^{II} , Ni^{II} , Se^{IV} , Nb^V , Ta^V , 2 mg/20 ml; Co^{II} , Fe^{II} , Fe^{III} , Cr^{III} , Zr^{IV} , Cr^{VI} , W^{VI} , 1 mg/20 ml; Au^{III} , V^V , 0.5 mg/20 ml; Pd^{II} , Ru^{III} , Ir^{III} , Pt^{IV} , Os^{VIII} , 0.25 mg/20 ml. Mo, 0.1 mg/20 ml, interferes.

Stability, reproducibility, Beer's law obedience and Sandell's sensitivity of the complex

The metal complex is quite stable; the absorbance remains unchanged even after 2 h. The results obtained are highly reproducible, with a standard deviation of 0.001. Beer's law is obeyed in the range of 0–4 $\mu\text{gRe ml}^{-1}$. The optimum concentration range that can be measured accurately, as evaluated from the Ringbom plot, is 1.12–3.98 ppm of Re (Fig. 2). Molar absorptivity, specific absorptivity and Sandell's sensitivity of the complex are $2.98 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, $1.60 \times 10^{-1} \text{ ml g}^{-1} \text{ cm}^{-1}$ and $0.0062 \mu\text{gRe cm}^{-2}$, respectively.

Stoichiometry of the complex

The ratio of rhenium, thiocyanate and potassium hexacyanoferrate(II) in the extracted species is determined by Job's method of continuous variations² as modified by Vosburgh and Cooper³ for the two-phase system.

Re:thiocyanate. x ml of $1.613 \times 10^{-3} \text{ M}$ solution of KReO_4 and $(5-x)$ ml of equimolar solution of KSCN are mixed and extraction is performed under conditions of the procedure. The absorbance of the metal complex is measured at 400 and 440 nm. The graph plotted between different mole fractions of Re and their

Fig. 3 Continuous variation of rhenium and thiocyanate. Concentration of KReO_4 , $1.613 \times 10^{-3} \text{ M}$; KSCN , $1.613 \times 10^{-3} \text{ M}$. Solvent, isopentyl alcohol. Curve A, at 400 nm; B, 440 nm.

Fig. 4 Mole ratio method. Concentration of KReO_4 , $1.613 \times 10^{-3} \text{ M}$; KSCN , $1.613 \times 10^{-3} \text{ M}$. Re for each operation, 1 ml of $1.613 \times 10^{-3} \text{ M}$. Solvent, isopentyl alcohol. Curve A, at 400 nm; B, 440 nm.

corresponding absorbance values indicates that Re and thiocyanate are present in the ratio of 1:3 (Fig. 3).

This fact is further supported by the mole ratio method.⁴ Here, the volume of rhenium solution is kept constant (1 ml of $1.613 \times 10^{-3} \text{ M}$) and the content of equimolar solution of thiocyanate is varied from 0 to 5 ml. After this procedure, the absorbances are measured and a graph is plotted between different mole ratios and their corresponding absorbance values, as shown in Fig. 4. This plot also gives the same ratio.

Re:potassium hexacyanoferrate(II). The ratio of rhenium to potassium hexacyanoferrate(II) in the metal complex is found to be 1:1 by Job's method, using equimolar solutions ($2.69 \times 10^{-4} \text{ M}$) of both the variables. While maintaining other conditions as per procedure, we performed the extraction and plotted the graph from the

Fig. 5 Continuous variation of rhenium and potassium hexacyanoferrate(II). Concentration of KReO_4 , 2.69×10^{-4} M; potassium hexacyanoferrate(II), 2.69×10^{-4} M. Solvent, isopentyl alcohol. Curve A, at 400 nm; B, 440 nm.

Fig. 6 Mole ratio method. Concentration of KReO_4 , 2.69×10^{-4} M; Potassium hexacyanoferrate(II), 2.69×10^{-4} M. Re for each operation, 1 ml of 2.69×10^{-4} M. Solvent, isopentyl alcohol. Curve A, at 400 nm; B, 440 nm.

data obtained (Fig. 5). The same result is confirmed by the mole ratio method (Fig. 6).

The above studies allow us to conclude that Re, potassium hexacyanoferrate(II) and thiocyanate are present in the ratio of 1 : 1 : 3 in the extracted species.

In conclusion, the proposed method for the trace determination of rhenium is quite sensitive and free from the interference of 31 analytically important elements, including Pt-metals while Mo^{VI} interferes. The validity of the method was tested by satisfactory analysis of a number of samples. The method is highly reproducible and compares favorably with the existing methods⁵⁻⁹ of rhenium determination.

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