An Improved Thiocyanate Method for the Determination of Rhenium

V YATIRAJAM, SIRPAL KHAIRA (neé SIRPAL SAIKHON) &
L R KAKKAR*

Department of Chemistry, Kurukshetra University, Kurukshetra
132119

An improved thiocyanate method has been developed for the determination of rhenium. In the presence of a reductant ($SnCl_2.2H_2O$), rhenium forms a yellow complex with thiocyanate in acid media, which is extractable into tribenzylamine-chloroform. This extract is then treated with acetone and heated for 1 min on a water-bath at $\sim 70°C$ and is then allowed to stand for 1 hr. Its absorbance is measured at 430 nm (λ_{max}) against the corresponding reagent blank. The tolerance limits of a number of ions have been studied. The method has a Sandell's sensitivity of 0.0051 $\mu g/cm^2$ and obeys Beer's law in the range 0-4.8 μg Re/ml. The validity of the method has been tested by analysis of several synthetic mixtures.

In the oft used thiocyanate method employed for the determination of rhenium[1], several modifications[2-6] have been suggested from time to time to increase its usefulness and widen its scope. Though some success has been claimed, the method still needs attention as far as its sensitivity is concerned.

In the present note, an improvement has been suggested in the existing thiocyanate method by extracting the rhenium-thiocyanate complex into tribenzylamine-chloroform in acid medium. The improved method is highly sensitive and has been used for the analysis of rhenium in several synthetic mixtures.

A stock solution of rhenium containing 1 mg/ml of the metal ion was prepared by dissolving an accurately weighed amount of potassium perrhenate (Specpure, Johnson-Matthey) in distilled water. Working solutions containing 50 $\mu g/ml$ of rhenium were prepared by appropriate dilution of the stock solution. Solutions of other ions were prepared by dissolving their salts (BDH) in water or dilute hydrochloric acid and were standardised by conventional methods[7].

Stannous chloride solution (20%) was prepared by taking stannous chloride in 20 ml of 1:1 HCl and heating till a clear solution was obtained. The volume was made upto 100 ml with distilled water.

A 1.5% solution of tribenzylamine (Fluka, extra pure >99%) was prepared in distilled chloroform (BDH).

Absorbance measurements were done with a Beckmann DU-2 Model Ultraviolet spectrophotometer using 1 cm cells.

Synthetic mixtures were prepared from solutions of rhenium and other elements in suitable amounts.

Procedure

To a solution containing $\leqslant 120$ μg rhenium in a 100 ml separatory funnel, were added 3 ml of 10 M HCl, 1 ml of 20% aqueous potassium thiocyanate solution and 1.5 ml of 20% stannous chloride solution. The contents were diluted to 20 ml, gently stirred and allowed to stand for 4 min. The yellow coloured complex formed was extracted by equilibrating once for 3 min with an equal volume of 1.5% tribenzylamine (TBA) solution in chloroform. The solvent layer was then drawn off into a conical flask containing 3 ml of acetone. The solution was covered and heated for one minute at $\sim 70°C$ on a water-bath. It was allowed to stand for 1 hr and then filtered to remove any suspended droplets of water, into a 25 ml volumetric flask. The volume was made up to the mark with pure chloroform. The absorbance of the complex was measured at 430 nm against the corresponding reagent blank.

In acid medium, rhenium is reduced to lower valence with stannous chloride which forms a yellow complex with thiocyanate. The coloured species is quantitatively extracted into tribenzylamine-chloroform and the absorbance is measured at 430 nm in presence of acetone.

Optimum conditions for the estimation

The absorbance of the complex is influenced by change in operative parameters as shown in Table 1. It is maximum in the acid range 1.25-1.75 M. Further increase in acidity (> 1.75 M) results in lowering of absorbance. A constant value of 0.395 is obtained for 1.0-1.5 ml of the thiocyanate reagent. At [thiocyanate] > 1.5 ml, there is a slight fall in absorbance, which might be due to change in the composition of the species into one of lower absorbance. Optimum value of stannous chloride concentration is 1.25-2.0 ml in 20 ml volume.

The absorbance of the complex shows a gradual increase with time up to 3 min and thereafter becomes constant; hence 4 min were allowed for colour development. It is necessary to leave the aqueous solution undisturbed before equilibrating with the extractant failing which the absorbance has a low value.

Table 1—Dependence of Rhenium-Thiocyanate Absorbance* on Various Parameters

[HCl]ᵃ, M	0.1	0.5	1.0	1.25	1.5	1.75	2.0
(Absorbance)	(0.215)	(0.300)	(0.360)	(0.395)	(0.395)	(0.390)	(0.360)
[KCNS]ᵇ (20%), ml	0.2	0.5	1.0	1.5	2.0		
(Absorbance)	(0.100)	(0.360)	(0.395)	(0.397)	(0.386)		
[SnCl₂.2H₂O]ᶜ (20%), ml	0.20	0.75	1.0	1.25	1.5	1.75	2.0
(Absorbance)	(0.090)	(0.377)	(0.385)	(0.395)	(0.395)	(0.395)	(0.395)
Colour dev. timeᵈ, min	0.5	1	3	4	5	7	8
(Absorbance)	(0.365)	(0.380)	(0.395)	(0.395)	(0.391)	(0.391)	(0.391)
Equilibration timeᵉ, min	1	2	3	4	6		
(Absorbance)	(0.310)	(0.389)	(0.395)	(0.395)	(0.394)		
[TBA]ᶠ, %	0.0	0.5	1.0	1.5	2.0	3.0	4.0
(Absorbance)	(0.00)	(0.306)	(0.394)	(0.395)	(0.395)	(0.361)	(0.357)
[Acetone]ᵍ, ml	1	2	3	3.5	4	5	
(Absorbance)	(0.342)	(0.378)	(0.395)	(0.395)	(0.383)	(0.372)	
Heating timeʰ, min	0	1	2	3	4	5	
(Absorbance)	(0.310)	(0.400)	(0.397)	(0.397)	(0.397)	(0.397)	

(a) Re = 50 μg, KCNS = 1 ml, SnCl₂.2H₂O = 1.5 ml, colour development time = 7 min, aq. vol. = 20 ml, solvent vol. = 10 ml, No. of extraction = 2, equilibration time = 3 min, acetone = 2 ml, heating time = 3 min; (b) HCl = 1.5 M; (c) KCNS = 1 ml; (d) SnCl₂.2H₂O = 1.5 ml; (e) colour development time = 4 min; (f) equilibration time = 3 min; (g) TBA concentration = 1.5%; Aq. vol. = solvent volume = 20 ml, No. of extraction = 1; (h) acetone = 3 ml.

*Initial conditions as under (a), and subsequent ones for the rest.

The absorbance is influenced by the nature of the extractant. Chloroform alone does not extract the complex at all. Tribenzylamine in chloroform gives an absorbance value of 0.395, whereas in carbon tetrachloride, it is 0.16. Turbidity results if benzene is used as a diluent for the reagent. Tributyl phosphate in chloroform gives an absorbance of only 0.21. Tribenzylamine in chloroform was, therefore, chosen as the optimum extractant mixture. With 1-2% TBA in CHCl₃, the absorbance was 0.395. Increasing reagent concentration showed a slight decline in absorbance value which may be attributed to the formation of some other species having lesser extractability. Rhenium is quantitatively transferred to the solvent in a single extraction under the aforementioned optimum conditions.

It has been observed that the rhenium-thiocyanate complex does not give a constant absorbance value when extracted into TBA-CHCl₃. There is a gradual increase in the reading with time, which however, becomes constant only after more than 3 hr. It was found that if acetone was added to the solvent after extraction, constancy in the absorbance reading was achieved after 1 hr. In addition to acetone, several other reagents like methylene chloride, 1,4-dioxane, rectified spirit, methyl cyanide, nitrobenzene and nitromethane were tried, but these were not successful. Maximum absorbance was observed for 3-3.5 ml of acetone.

The effect of heating time of the complex on the absorbance was also studied. Without heating i.e. at room temperature, the absorbance was 0.310 which increased to 0.395 on heating for 1 min or more. There was hardly any loss of chloroform or acetone while heating on a water-bath at ∼70°C.

It is clear from the above data that for an aliquot containing 120 μg Re, the optimum conditions of determination are: 1.5 M HCl, 1 ml potassium thiocyanate (20%), 1.5 ml stannous chloride (20%) in 20 ml aqueous volume, 4 min standing time for colour development of the complex and equilibrating once with an equal volume of 1.5% tribenzylamine in chloroform for 3 min. The absorbance was measured after the addition of 3 ml acetone to the extract, heating for 1 min and allowing it to stand for 1 hr after making up the volume to 25 ml.

The effect of diverse ions on the absorbance of rhenium-thiocyanate complex extracted was studied. Chloride, acetate (12.5 mg/ml); sulphate, tartrate (15 mg/ml); oxalate (5 mg/ml); and phosphate (2 mg/ml) do not affect the determination. Nitrate (2 mg/ml) and thiourea (1 mg/ml) decrease the absorbance whereas EDTA (5 mg/ml) increases it slightly and fluoride (2.5 mg/ml) enhances it considerably. The amounts shown in parentheses are for the sodium salts of the anions. W(VI), U(VI), Ni(II), Mn(II) (0.5 mg/ml); Al(III), Mg(II), Pb(II), Zn(II), Ca(II), Cd(II), Cu(II) (0.25 mg/ml); Cr(III, VI) (0.15 mg/

Table 2—Analysis of Synthetic Mixtures and Alloys by the
Proposed Method

Sl. No.	Sample Composition		Re found (μg)
	Matrix*	Re (μg)	
1.	Ni(10)	30	29.5
2.	W(10)	30	28.5
3.	U(10)	20	18.0
4.	Mg(5)	30	28.0
5.	V(0.1)	25	25.2
6.	Ru(0.1)	10	10.3
7.	Ca(5), Cd(5), Zn(5), Ru(0.05), Al(5)	25	24.0
8.	Ni(7), Mn(3), U(4)	25	24.0
9.	Mn(5), Fe(0.1), Ni(10), Mg(4), Cr(0.1)	20	19.0
10.	W(4), U(5), V(0.1)	20	20.0
11.	Nickel alloy (C = 0.03%, Si = 0.01%, S = 0.003%, P = 0.01%, Fe = 0.06%, Mn = 0.005%)	1%	1.045%
12.	Nickel alloy (Si traces S = 0.03%, C = 0.03%, Fe = 0.06%, P = 0.01%, Mn = 0.005%, Co = 0.008%)	1%	1.05%

*Figure in the bracket indicates the amount of the metal ion in mg.

ml); V(V), Ru(III), Fe(II, III) (0.1 mg/ml) do not give any absorbance. Mo(VI) and Pd(II) interfere and need prior separation.

The method is highly sensitive with a molar absorptivity of 3.7×10^5 l mol^{-1} cm^{-1} corresponding to a Sandell's sensitivity of 0.0051 μg/cm^2 and compares well with the existing methods of rhenium determination. Beer's law is obeyed in the range 0-4.8 μg Re/ml and the results obtained are reproducible. Rhenium, in trace amounts, can be determined satisfactorily by this method in presence of several analytically important elements, especially W(VI), Cr(VI, III), V(V), Ru(III), and Fe(III, II) which interfere seriously in the determination of the former. Further, the usefulness of the method was tested by the analysis of several synthetic mixtures (Table 2), the last two of which correspond to known alloys of rhenium. The results obtained are in good agreement with the amount of the metal ion added initially to the sample (Table 2).

References

1 Sandell E B, *Colorimetric determination of traces of Metals*, 3rd Edn (1959) 755.
2 Hiskey C F & Meloche V W, *Ind Eng Chem Anal Edn*, 12 (1940) 503.
3 Melaven A D & Whetsel K B, *Anal Chem*, 20 (1948) 1209.
4 Hoffman J I & Lunddle G E F, *J Res Nat Bur Standards*, 23 (1939) 466.
5 Savariar C P & Hariharan T R, *J Indian chem Soc*, 55(4) (1978) 349-51.
6 Shinde V M, *Indian J Chem A*, 23A(11) (1984) 965.
7 Kodama K, *Methods of quantitative inorganic analysis* (Interscience, New York).1963.
8 Gonser B W, *Rhenium* (Elsevier, Amsterdam, New York) 1962, 4.