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The Simultaneous Extraction and Spectrophotometric Determination of Rhodium(III) with 2-Thenoyltrifluoroacetone

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A method has been described for the extractive spectrophotometric determination of rhodium(III) with 2-thenoyltrifluoroacetone (TTA) in an acetone-xylene mixture. The bright yellow rhodium(III)-TTA chelate solution in an acetone-xylene solvent mixture obeys Beer's law over the concentration range of 1.95—19.5 μg. of rhodium per ml. Around pH 6.0 quantitative extraction is possible with 0.015 M TTA - acetone - xylene. The colour of the complex is quite stable up to 72 hr. Rhodium(III) can be extracted in the presence of a large number of ions.

Of the β-diketones used as chelating agents, 2-thenoyltrifluoroacetone (TTA) has proved to be one of the most versatile chelating and extracing agents for the liquid-liquid extraction and spectrophotometric determination of numbers of elements.[1] During the solvent extraction studies of palladium[2] with this reagent, it was found that rhodium(III) also gives a bright yellow-coloured complex in a TTA-acetone mixture in the presence of xylene.

The separation of rhodium from iridium, lanthanum, cerium and zirconium was accomplished by using pyridine.[3] Similarly, the pyridine-thiocyanate complex[4] in hexone was measured spectrophotometrically at 380 mμ. The extractive separation of rhodium from iridium in a hydrobromic-perchloric acid solution was carried out with isopentyl alchool.[5] The separation of rhodium(III) from platinum and palladium was done with diantipyrylpropyl methane.[6] Linder[7] attempted the extraction of rhodium with 0.50 M TTA - acetone - benzene solutions, but the method proved to be laborious and time consuming. So far no systematic work has been carried out on the simultaneous extraction and spectrophotometric determination of rhodium with TTA.

In this paper a method will be described for the liquid-liquid extraction of rhodium at micro-levels with a 0.015 M TTA - acetone - xylene solution. The optinum conditions, as established from the critical investigation of various influencing factors, will also be presented.

Experimental

Apparatus and Reagents.—A type C♯ϕ 4 quartz spectrophotometer with 10-mm. quartz cells and a Cambridge pH meter (Marshal model were used).

2-Thenoyltrifluoroacetone (B. D. H. Anal R), about a 0.015 M solution in acetone, was used. A stock solution of of rhodium(III) was prepared by dissolving one gram of $RhCl_3 \cdot 3H_2O$ (Johnson Matthey and Co., Ltd., London) in 500 ml. of water containing ~0.5% hydrochloric acid. The solution, on standardization,[8,9] was found to contain 78.2 μg. of rhodium per ml.

General Procedure.—An aliquot of a rhodium chloride solution containing about 78.2 μg. of rhodium per ml. was taken. Then 0.1 ml. of 60 per cent perchoric acid was added to the solution. The pH of the solution was then adjusted to the desired pH by the addition of 0.01 M hydrochloric acid or 0.01 M sodium hydroxide. The final volume of the aqueous phase was made up to 25 ml. in each case.

During the studies of the effect of salting-out agents or diverse ions, each one of them was added to the solution before the adjustment of the pH value.

The solution, after adjustment to pH=6.0 unless otherwise specified, was transfered to a 250-ml. separatory funnel. Then 10 ml. of 0.015 M TTA in acetone was added to it. Immediately after the addition of the reagent, 10 ml. of xylene was added to the mixture. After the separatory funnel had been properly stoppered, it was shaken briskly for about 10 min. The layers were then allowed to settle and separate. The organic phase was carefully withdrawn to a 10-ml. volumetric flask. The absorbance of a bright yellow-coloured complex was measured at 430 mμ against the

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1) S. M. Khopkar and A. K. De, *J. Sci. and Ind. Res.*, **21A**, 131 (1962).

2) A. V. Rangnekar and S. M. Khopkar, This Bulletin, **38**, 1696 (1965).

3) N. E. Ballou, "Radiochemical Studies—The Fission Products," McGraw Hill Book Co. Inc., New York (1951), p. 1563.

4) J. H. W. Forsythe, R. J. Magee and C. L. Wilson, *Talanta*, **3**, 330 (1960).

5) G. G. Tertipis and F. E. Beamish, *Anal. Chem.*, **34**, 623, (1962).

6) A. I. Busev and V. A. Akimov, *Zh., Analit. Khim.*, **18**, 610 (1963); *Chem. Abstr.*, **59**, 4527 (1963).

7) M. Linder, U. S. Atomic Energy Commission Report UCRL-4377.

8) A. K. De, "Separation of Heavy Metals," Pergamon Press Ltd., London (1961), p. 234.

9) K. Watanabe, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **77**, 1008 (1956).

reagent blank. The amount of rhodium present was calculated from the Beer's law plot.

The reagent blank was prepared as follows, 10 ml. of 0.015 ml. TTA - acetone was equilibrated with 10 ml. of xylene. The phases were then allowed to settle and to separate. The organic phase was used directly as the reagent blank.

Results and Discussion

Absorption Spectra.—The absorption spectrum of the solution of the rhodium(III)-TTA complex (Rh=7.60×10^{-6} M) is shown in Fig. 1. The bright yellow rhodium(III)-TTA solution absorbs strongly around 420 mμ. The reagent blank at this wavelength also shows some absorbance. The absorbance of the complex gradually decreases, until it becomes negligible beyond 480 mμ. The reagent itself shows an insignificant absorbance at 430 mμ; hence, all the absorbance measurements were carried out at this wavelength. The molecular extinction coefficient at 430 mμ, on the basis of rhodium contents, is 276±9.5. On account of strong absorbance of the reagent itself, tests were not made below 410 mμ.

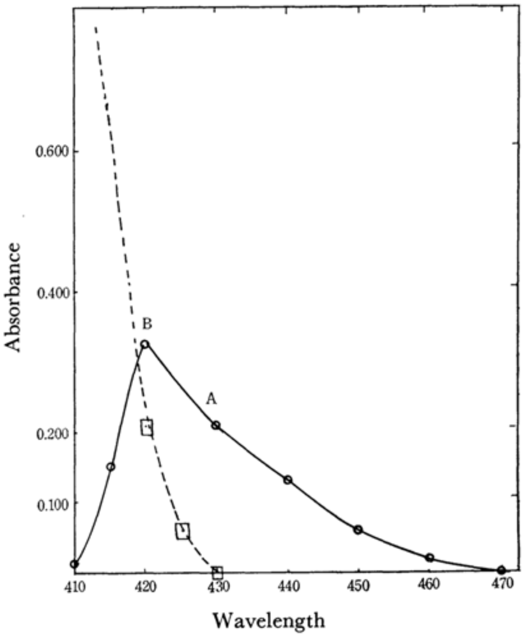

Fig. 1. Absorption spectra.

A. Absorption spectrum of Rh(III) - 2-Thenoyltrifluoroacetone chelate in acetone-xylene mixture. Rh(III)=7.60×10^{-6} M, TTA=1.5×10^{-3} M, pH=6.0 versus reagent blank.

B. Absorption spectrum of the reagent blank solution versus solvent mixture.

The Effect of the Amount of Acetone in the Solvent Mixture.—The complex of rhodium with TTA is soluble in acetone and, although very little, in xylene. The addition of xylene to the aqueous phase extracts the complex into the organic phase. Acetone is miscible only in the aqueous phase. The solubility of the acetone in the organic phase at the pH of extraction is practically negligible. Hence, for all practical purposes, it may be assumed that the volume of an organic phase, namely, 10 ml. of xylene, is the same both before and after the extraction of rhodium.

For the clean-cut separation of two layers, the ratio of acetone to xylene must, however, be controlled. From the experimental observations it was found that the optimum ratio of acetone to xylene is 1 : 1 (by volume). If the ratio is changed from 1 : 1 to 1 : 2 or 1 : 3 or even more at the time of extraction, the enhanced volume of xylene in the organic phase produces turbidity and inhibits the colorimetric determination of rhodium.

The Effect of the pH Value.—The solvent extraction behaviour of the rhodium(III)-TTA system was studied over the pH range from 1.0 to 7.0. On plotting the graph of the percentage extraction as the function of pH (Fig. 2), it was observed that the extraction commences around pH ~2.0; then it steadily increases, becoming quantitative around pH=6.0. In the pH region of 2.5—3.5, the extraction is quite large, but incomplete, while in the pH region from 5.2 to 6.2 the extraction tends to be complete. It is possible to extract rhodium(III) quantitatively at pH 6.0 with 0.015 M TTA - acetone in the presence of

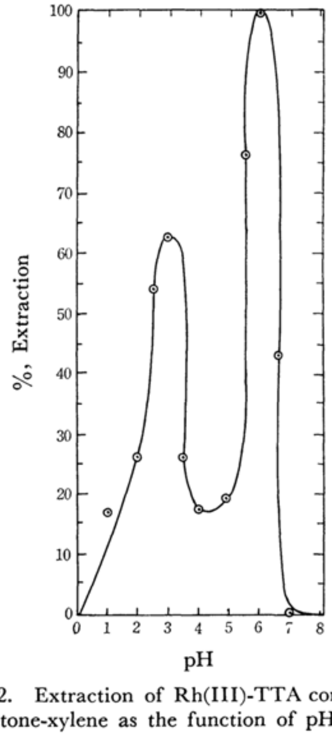

Fig. 2. Extraction of Rh(III)-TTA complex with acetone-xylene as the function of pH.

xylene. It is not worthwhile attempting extraction at pH >6.5, however, as rhodium may precipitate as the hydroxide. Furthermore, the extraction curve drops sharply beyond pH 6.5 and terminates at pH 7.0; the pH of the solution remains unaltered after extraction in the pH region of 1.0—7.0. Moreover, the reagent, TTA, possesses the advantage of being very effective in the acid regions as compared with other β-diketones.10)

The Effect of Salting-out Agents.—Such salting-out agents as chlorides of magnesium, barium, sodium and potassium were tested in order to observe their effect on the extraction of rhodium by TTA (Table I). It was found that none of them have a pronounced effect upon the extractability of rhodium. The effect of the addition of different volumes of 60% perchloric acid on the extractability of rhodium was also studied. The presence of perchloric acid in the aqueous phase enhances the extraction. This may be explained as follows:—

TABLE I. EFFECT OF SALTING-OUT AGENTS

Salting-out agent	Concn.	Absorbance at 430 mμ	% Extraction
None	—	0.210±0.010	100
$MgCl_2$	1 M	0.155	73.8
$BaCl_2$	1 M	0.100	47.6
NaCl	1 M	0.210	100
KCl	1 M	0.100	47.6
$HClO_4$ 60%	0.10 ml.	0.210	100
	0.15 ml.	0.195	92.8
	0.2 ml.	0.195	92.8

i) It might provide a higher concentration of the complexing anion in the system, a concentration which, by mass action, would increase the concentration of the complex and enhance the extraction, or

ii) The dielectric constant of the aqueous phase might decrease with an increase in the ionic concentration, or

iii) By binding of the water molecules by the anions, it might become unavailable as a free solvent, or

iv) It may have a pronounced effect upon the activity coefficient of the ions participating in the formation of the complex.

In general, large ionic size and the charge of an ion such as the perchlorate ion play an important role in enhancing the extraction.

Beer's Law Plot.—The absorbance of different amounts of rhodium(III) extracted at pH 6.00 were noted against the reagent blank at 420, 430, and 440 mμ. The results in Table II show that the system conforms to Beer's law at 430 mμ over the concentration range of 1.95—19.5 μg. of rhodium per ml.

TABLE II. BEER'S LAW

Rhodium(III) taken, μg.	420 mμ	430 mμ	440 mμ
62.56	0.260	0.170	0.120
78.20	0.310	0.210	0.130
101.66	0.430	0.280	0.200
117.30	0.490	0.320	0.250

The Stability of the Colour of the Complex.—The absorbance of an acetone-xylene solution of a rhodium-TTA complex was measured at 430 mμ at lapsed times of 1, 2, 4, 7, 16, 24, 48, 72 and 96 hr. The corresponding absorbances were 0.210, 0.210, 0.210, 0.210, 0.210, 0.210, 0.210, 0.215 and 0.220. This clearly shows that the colour of the complex is quite stable up to 72 hr. It undergoes about a 2.1% decomposition beyond this time.

The Effect of Different Concentration and Volumes of the Reagent.—The effect of varying volumes as well as varying concentrations of the reagent on the extraction behaviour was studied. The results in Table III show that in no case does acetone play a vital role in influencing the extractability of rhodium, either at varying volumes and at varying concentrations of the reagent. It can be also seen that the use of 5, 10 or 20 ml. of 0.015 M TTA gives a constant value for the absorbance when the rhodium concentration is kept constant. This amply supplements the above observation.

TABLE III. EFFECT OF DIFFERENT VOLUME AND CONCENTRATION OF THE REAGENT
(Rh=78.2 μg., pH=6.0)

TTA concn. M	TTA added ml.	Absorbance at 430 mμ
0.015	10	0.210±0.010
0.015	20	0.210
0.015	5	0.210
0.015	2	0.0
0.0015	10	0.030
0.0075	10	0.080
0.010	10	0.150
0.025	10	0.220
0.050	10	0.235

Since the absorbance at 0.015 M TTA is quite large, it is recommended that this concentration be used in all the determinations in preference to the higher concentration of the reagent. Moreover, the latter are also uneconomical.

The use of lower concentrations, such as 0.0075 and 0.0015 M, are unsuitable, as very little of the reagent is actually available for the complete

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10) G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry," John Wiley & Co., New York (1957), p. 27.

TABLE IV. DIVERSE IONS
(Rh(III)=78.2 μg.; pH=6.0, TTA=0.015 M)

Foreign ion	Added as	Amount added	Absorbance at 430 mμ
None	—	—	0.210 ±0.010
Tl^+	Tl_2SO_4	150	0.240a)
Pb^{2+}	$Pb(CH_3COO)_2$	300	0.205
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	78	Colourb)
Pd^{2+}	$PdCl_2 \cdot 2H_2O$	78	Coloura)
Fe^{3+}	$FeCl_3$	78	Colourb)
Al^{3+}	$AlCl_3 \cdot 3H_2O$	78	0.220
Cr^{3+}	$CrCl_3 \cdot 6H_2O$	39	Coloura)
Th^{4+}	$Th(NO_3)_4$	78	0.200
UO_2^{2+}	$UO_2(NO_3) \cdot 2H_2O$	39	Colour
Ce^{4+}	$Ce(SO_4)_2$	39	Colour
Be^{2+}	$Be(NO_3)_2$	150	0.215
Zn^{2+}	$ZnSO_4 \cdot 7H_2O$	78	0.180a)
Mn^{2+}	$MnCl_2 \cdot 2H_2O$	39	Coloura)
Co^{2+}	$Co(NO_3)_2 \cdot 2H_2O$	39	Colourb)
Ni^{2+}	$NiSO_4 \cdot 5H_2O$	39	Colourb)
Ca^{2+}	$CaCl_2 \cdot 2H_2O$	75	0.195
CH_3COO^-	CH_3COONH_4	150	0.220c)
Malonate^{2-}	$CH_2(COOH)_2$	75	0.215
EDTA^{3-}	EDTA (disodium salt)	80	0.210
$C_2O_4^{2-}$	$H_2C_2O_4 \cdot 2H_2O$	78	0.210
PO_4^{3-}	Na_2HPO_4	78	0.215
$S_2O_3^{-2}$	$Na_2S_2O_3 \cdot 5H_2O$	80	0.210

a) Interference eliminated by complexation with EDTA.

b) Interference eliminated by formation of cyanide complexes.

c) Interference eliminated by anion exchange resin.

complexation of the metal ion, resulting in incomplete extraction.

The Effect of Diverse Ions.—The effect of the presence of diverse ions on the extraction of rhodium was also studied. It was seen that lead, aluminum, beryllium, thorium, thiosulphate, EDTA(-disodium salt), acetate, oxalate, phosphate showed no interference (Table IV). However, the ions giving characteristic colour reactions with TTA, such as copper, cerium, uranium, iron, cobalt, nickel and chromium, interfere. The interferences due to common cations, such as copper, cobalt, iron, and nickel, can be eliminated by converting them into suitable anionic cyanide complexes, which, in general, are not extracted by this reagent. Similarly, the interferences due to such ions as thallium, chromium, zinc, and manganese can be eliminated by converting them to suitable anionic EDTA complexes. The interferences due to a few anions can be eliminated by passing the solution over a strongly basic anion exchange resin such as Dowex 1-X8 before the extraction step.

About 78.2 μg. of rhodium was taken up and extracted as per the "general procedure" at pH 6.0. The organic phase was separated, and the absorbance of a bright yellow-coloured complex was measured at 430 mμ. From eight runs with 78.2 μg. of rhodium(III), the absorbance noted was 0.210+0.010. The standard deviation was ±1.2%. The method permits the simultaneous extraction and spectrophotometric determination of rhodium within 30 min. As little as 76 γ of rhodium per ml. can be detected.