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Extraction-Photometric Determination of Osmium with Thenoyltrifluoroacetone

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The study of the liquid-liquid extraction of some platinum group elements (A. V. Rangnekar and S. M. Khopkar, *Bull. Chem. Soc. Japan,* **38**, 1696 (1965); **39**, 2169 (1966)), with fluorinated β-diketones showed that, osmium reduced to trivalent state with hydroxylamine hydrochloride forms a red chelate with 2-thenoyltrifluoroacetone, TTA. The chelate is readily extracted in benzene giving strong absorbance at around 440 mμ.

The thiocarbonilide¹⁾ complex of osmium is extracted with ether, where as complex with ephedrine hydrochloride²⁾ was extracted in carbon tetrachloride. Thiourea³,⁴⁾ was used for extraction and colorimetric determination of osmium. Such complex was extracted in chloroform and measured at 480 mμ. The osmium was found to be in the trivalent state with composition of the extractable⁵⁾ species as $[Os(NH_2{-}CS{-}NH_2)_6]^{3+}$. The other extracting agents include; thiosemicarbazide,⁶⁾ 1-naphthylamine -3, 5, 7-trisulphonic acid,⁷⁾ mercaptobenzimidazole⁸⁾ and *o*-(β-benzoylthiourido)benzoic acid.⁹⁾ Unfortunately these methods

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1) W. Singleton, *Ind. Chem.*, **3**, 121 (1927).

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3) E. B. Sandell, *ibid.*, **16**, 342 (1944).

4) G. H. Ayres and W. N. Wells, *Anal. Chem.*, **22**, 317 (1950).

5) R. D. Sauerbrunn and E. B. Sandell, *J. Am. Chem. Soc.*, **75**, 3554 (1953).

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are not rapid. An attempt is made in this paper to present a rapid method for the extraction-photometric determination of osmium at micro-levels with TTA.

Experimental

Apparatus and Reagents. A type SP-4 quartz spectrophotometer, Cambridge pH meter, wrist action flask shaker. TTA (E. Merck and Co.) 0.015 M solution in benzene. A stock solution of osmium was prepared from osmic acid as by Ayres' method.[4] On standardisation[3,10] it was found to contain 58.8 μg of osmium per m*l*. Hydroxylamine hydrochloride (B. D. H) 5% aqueous solution.

General Procedure. An aliquot of the solution (294 μg of osmium) was taken, 10 m*l* of 5% hydroxylamine hydrochloride was added to reduce osmium to trivalent state, the pH of the solution was then adjusted to pH 4.5 with 0.01 N sodium hydroxide, and 0.01 N sulphuric acid. The final volume of the solution was made upto 20 m*l* and the solution was then transferred to separatory funnel. Ten millilitres of 0.015 M TTA-benzene was added and it was shaken for about 10 min. After allowing the solution to settle and separate, organic phase was stripped into 10 m*l* volumetric flask. The absorbance of the colored complex was measured at 440 mμ. The amount of osmium was computed from the calibration curve.

Results and Discussion

Absorption Spectrum. The absorption spectrum of Os(III)-TTA complex (Os$=1.545\times10^{-4}$ M) shows strong absorbance at 430 mμ (Fig. 1). Although the reagent blank shows significant absorbance at 420 mμ, it is negligible at 430 mμ. All absorbance measurements were therefore made at 440 mμ. The molar absorptivity is 1.42×10^2 at 440 mμ on the basis of osmium contents.

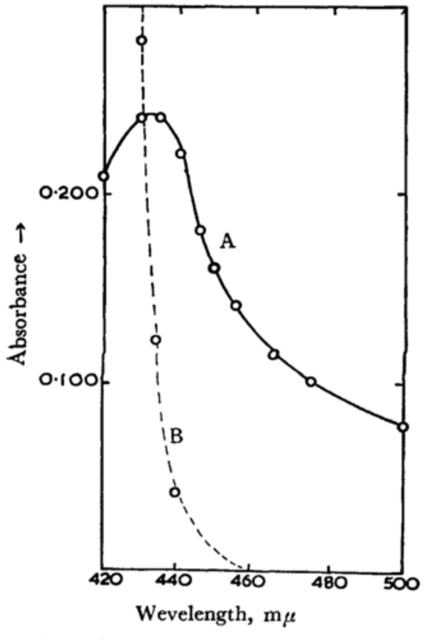

Fig. 1. Absorption spectra of osmium-TTA complex.

A Os(III)-TTA complex *vs.* reagent blank Os(III)$=1.545\times10^{-4}$ M at pH 4.5

B Reagent blank *vs.* benzene at pH 4.5 TTA$=1.5\times10^{-3}$ M

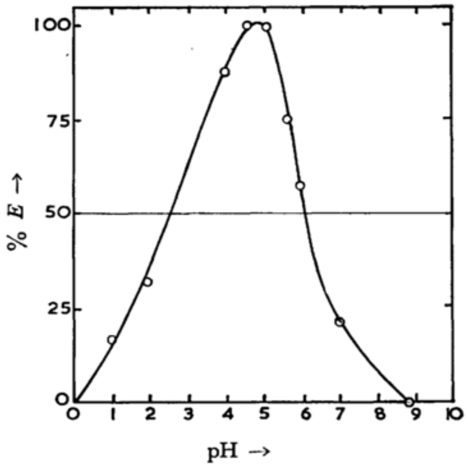

Fig. 2. Percentage extraction of osmium as the function of pH.

The Effect of pH Value. The extraction of osmium was carried out from pH 1.0—10.0 with TTA. (Fig. 2). The distribution ratio (*D*) was calculated as before[11,12] (Table 1). Between pH region of 3.5 to 5.5, more than 80% osmium is

TABLE 1. EXTRACTION AS THE FUNCTION OF pH

pH	*E* %	*D*
0.5	7.5	0.176
1.0	17.5	0.424
1.5	25.0	0.660
2.0	32.5	0.752
2.5	50.0	2.000
3.0	62.5	3.330
3.5	72.0	8.100
4.0	87.5	14.000
4.5	100.0	∞
5.0	100.0	∞
5.5	75.0	6.000
6.0	57.5	2.710
6.5	30.0	0.857
7.0	22.5	0.602
7.5	12.5	0.286
8.0	7.5	0.176
8.5	5.0	0.105
9.0	0.0	—

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[10] A. K. De, "Separation of Heavy Metals," Pergamon Press, London (1961), p. 237.

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

[12] A. V. Rangnekar and S. M. Khopkar, *ibid.*, **39**, 2169 (1966).

TABLE 2. BEER'S LAW CURVE

Osmium μg	Absorbance at mμ		
	430	435	440
58.8	0.040	0.040	0.045
88.2	0.055	0.070	0.110
117.6	0.100	0.100	0.095
176.4	0.140	0.140	0.135
235.2	0.190	0.180	0.175
294.0	0.230	0.230	0.220
352.8	0.270	0.270	0.265
441.0	0.300	0.300	0.320

TABLE 3. EFFECT OF REAGENT CONCENTRATION
Os=294 μg pH=4.5

Concentration M	Volume of reagent ml	Absorbance at 440 mμ
0.0015	10.0	0.000
0.0075	10.0	0.010
0.0150	5.0	0.100
0.0150	7.5	0.220
0.0150	10.0	0.220
0.0250	10.0	0.230
0.0500	10.0	0.240

extracted, but at pH 4.5 the extraction is quantitative. The $pH_{1/2}$ is 2.6 and 6.0.

Beer's Law Curve. The different amounts of osmium were extracted pH 4.5 (Table 2) and measured at 430, 435 and 440 mμ. The system conforms to Beer's law over the concentration range of 2.9 to 22 μg of osmium per ml at 440 mμ.

The Effect of Reagent Concentration. The osmium (294 μg) was extracted at pH 4.5 with varying concentration of the reagent (Table 3). The results indicate that 10 ml of 0.015 M TTA is quite adequate for quantitative extraction.

Stability of the Color. The absorbance of the colored complex was measured at lapsed interval of 30 min. Probably the complex decomposes after 6 hr. Therefore it is recommended to measure the absorbance within first 4 hr of complex formation.

Period of Shaking. The variation in period of shaking from 30 sec to 30 min revealed that the complex is quantitatively extracted within 10 min of shaking.

The Effect of Salting-out Agents. The sulphates of alkali and alkaline earth metals were used as the salting-out agents (Table 4). The results showed none of them have any pronounced effect upon the process of extraction.

TABLE 4. EFFECT OF SALTING-OUT AGENTS

Salting -out agent	Molarity M	Absorbance at 440 mμ
Li_2SO_4	1	0.120
	2	0.095
Na_2SO_4	1	0.220
	2	0.175
$(NH_4)_2SO_4$	1	0.140
	2	0.080
K_2SO_4	1	0.110
	2	0.100

TABLE 5. EFFECT OF DIVERSE IONS

Foreign ion	Added as	Amount added, μg	Absorbance at 440 mμ
None	—	—	0.220±0.010
Tl^+	Tl_2SO_4	3000	0.200
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	5000	Color
Cd^{2+}	$3CdSO_4 \cdot 8H_2O$	5000	0.220
Sb^{3+}	$SbCl_3 \cdot 3H_2O$	2500	0.220
Bi^{3+}	$Bi(NO_3)_3$	2000	0.150a)
Sn^{2+}	$Sncl_2 \cdot 2H_2O$	2500	0.220
Pt^{4+}	H_2PtCl_6	5000	0.220
Pd^{2+}	$PdCl_2 \cdot 2H_2O$	5000	0.210
Rh^{3+}	$RhCl_3 \cdot 3H_2O$	5000	0.210
Ir^{3+}	$IrCl_3 \cdot 3H_2O$	2500	0.195
An^{3+}	$HAuCl_4$	5000	0.210
Fe^{3+}	$FeCl_3$	5000	Colora)
U^{6+}	$UO_2(NO_3)_2 \cdot 2H_2O$	5000	Colorb)
Zr^{4+}	$Zr(NO_3)_4 \cdot 2H_2O$	1500	0.150b)
Th^{4+}	$Th(NO_3)_4 \cdot 4H_2O$	1500	0.150a)
Ce^{4+}	$Ce(SO_4)_2 \cdot 2H_2O$	5000	Colorb)
Zn^{2+}	$ZnSO_4 \cdot 7H_2O$	1800	0.210
Mn^{2+}	$MnCl_2 \cdot 4H_2O$	5000	0.210
Co^{2+}	$CoCl_2 \cdot 6H_2O$	5000	0.220
Ni^{2+}	$NiSO_4 \cdot 7H_2O$	500	0.195
Ca^{2+}	$CaCl_2 \cdot 2H_2O$	500	0.205
Mg^{2+}	$MgSO_4 \cdot 7H_2O$	500	0.205
Li^+	LiCl	1000	0.220
AsO_3^{3-}	Na_3AsO_3	5000	0.220
TeO_3^{2-}	Na_2TeO_3	1200	0.205
$Formate^-$	HCOOH	1000	0.200
$Tart^{3-}$	Tartaric Acid	5000	0.220
Cit^{3-}	Citric acid	5000	0.220
$Ascorb^{2-}$	Ascorbic acid	2500	0.225
$EDTA^{4-}$	EDTA(Na_2-salt)	5000	0.220

a) Interference eliminated by masking with EDTA at pH 2.0.

b) Interference eliminated by forming anionic complex with citrate at pH=6.0.

The Effect of Diverse Ions. The effect of the presence of several ions on the extraction behaviour was studied (Table 5). About 5 mg of cadmium, tin(II), platinum(IV), palladium, rhodium, iridium, gold, manganese, cobalt(II), arsenite, tartrate, citrate, and EDTA do not interfere. Similarly about 1 mg of antimony, zinc, lithium, tellurite, formate can be tolerated. The ions showing interference are thorium, bismuth, zirconium, cerium, uranium and iron; but their interference can be easily eliminated by complexation with suitable masking agents.

From twenty determinations, it was observed that the absorbance of the solution ranged from 0.210 to 0.230. The standard deviation is ±1.1%. As little as 1.33 μg of osmium per m*l* can be detected.

Summary

2-Thenoyltrifluoroacetone forms orange red chelate with trivalent osmium, the chelate which shows strong absorbance at 440 mμ. Beer's law is obeyed over the concentration range of 2.9 to 22 μg of osmium per m*l*. The color of the complex is stable. Large number of cations as well as anions are tolerated.

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