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Precipitation from Homogeneous Solution: I. Zirconium and Thorium Cupferrates; II. Nickel and Palladium Salicylaldoximates

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Summary

New methods are proposed for the precipitation of zirconium and thorium cupferrates and nickel and palladium salicylaldoximates from homogeneous solution. Zirconium cupferrate can be quantitatively precipitated from 7 to 10 vol. % sulfuric acid, dried at 100°C, and weighed as $Zr(C_6H_5N_2O_2)_4$, whereas thorium cupferrate, quantitatively precipitated at pH 1 to 3, must be ignited to ThO_2. The conventional method does not give quantitative precipitation of thorium cupferrate. Nickel is precipitated at pH 9 to 10.5 by salicylaldoxime in situ, dried at 120°C, and weighed as $Ni(C_7H_6O_2N)_2$, whereas palladium is precipitated from 2 to 2.5 vol. % sulfuric acid, dried at 110°C, and weighed as $Pd(C_7H_6O_2N)_2$. The interferences due to some commonly associated ions can be eliminated by appropriate masking agents.

The technique of precipitation from homogeneous solution (PFHS) first introduced by Bickerdike and Willard (*1*) and later developed by Gordon and others (*2*) has found considerable application in recent years for obtaining metal chelates in an extremely pure state which are stable and can be easily filtered and washed. The review article by Firsching (*3*) covers the literature up to early 1963.

Heyn and Dave (*4,5*) generated cupferron in the solution in situ by the reaction between phenylhydroxylamine and sodium nitrite. They determined copper as cupferrate by direct weighing, and titanium as dioxide by ignition of titanium cupferrate. None of the cupferrates except beryllium cupferrate (6) prepared by conventional precipitation can be directly weighed for analysis. We have extended the PFHS technique to zirconium and thorium cupferrates. Zirconium cupferrate is directly weighable after drying at 100°C, whereas thorium cupferrate, because of thermal instability, must be ignited to the oxide. This provides the basis for the gravimetric method reported in this paper for direct estimation of zirconium as cupferrate and for indirect estimation of thorium as oxide via cupferrate. By the conventional method, cupferron does not give quantitative precipitation with thorium, so it is of no use for the estimation of thorium. The PFHS technique is decidedly superior to the conventional method for cupferrate precipitation and estimation. The separation of zirconium and thorium from some of the commonly associated elements has been worked out.

Salicylaldoxime was first proposed by Ephraim (7) as a reagent for gravimetric determination of copper, and later the reagent was found useful for the determination of many metals. Riley (8) investigated the determination of nickel with salicylaldoxime and obtained good results. The precipitation of palladium with salicylaldoxime was reported to be quantitative in solutions containing free sulfuric acid (9). But the disadvantages of the reagent are its tendency to decompose and the formation of gelatinous precipitate which is difficult to filter. Pietrzak and Gordon (*10*) were the first to show the use of salicylaldoxime prepared from homogeneous solution, and they precipitated copper salicylaldoximate and obtained reproducible results.

In this paper we have utilized the in-situ generation of salicylaldoxime (by the reaction between salicylaldehyde and hydroxylamine hydrochloride) to precipitate nickel and palladium salicylaldoximates quantitatively in a much purer and more easily filterable form than that in the conventional method.

EXPERIMENTAL

Apparatus: Cambridge pH indicator.

Reagents:

Phenylhydroxylamine: Prepared from nitrobenzene (A.R.B.D.H.) according to the procedure of Vogel (*11*)

Sodium nitrite: E. Merck

Ammonium acetate: E. Merck

Salicylaldehyde: E. Merck

Hydroxylamine hydrochloride: E. Merck

Zirconium solution: 4.86 mg of zirconium/ml. Approx. 7 g of zirconium nitrate (E. Merck) was dissolved in 500 ml of 10 vol. % sulfuric acid. Zirconium was estimated as pyrophosphate (*12*).

Thorium solution: 8.06 mg of thorium/ml. Approx. 9 g of thorium nitrate, $Th(NO_3)_4 \cdot 4H_2O$ (E. Merck), was dissolved in 500 ml of water. Thorium was estimated as dioxide (*12*).

Nickel solution: 6.45 mg of nickel/ml. About 18 g of nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$ (E. Merck), was dissolved in 500 ml of water containing 2 ml of concentrated nitric acid. Nickel was estimated as dimethylglyoximate (*12*).

Palladium solution: 5.43 mg of palladium/ml. About 4 g of palladium chloride, $PdCl_2$ (E. Merck), was dissolved in 400 ml of water containing 13 ml of concentrated hydrochloric acid. Palladium was estimated as dimethylgyloximate (*12*).

Buffer solution: pH 10 to 10.5 (ammonia–ammonium chloride)

All other reagents were of reagent grade, unless otherwise mentioned.

General Procedure

The conditions of precipitation of the cupferrates and salicylaldoximates and the analytical procedures are summarized in Tables 1 and 2.

RESULTS AND DISCUSSION

Nature of the Cupferrate Precipitates

The precipitate obtained directly from the conventional procedure cannot be dried and weighed because of the irregular composition. Furthermore, the precipitate is contaminated with excess reagent, which leads to subsequent decomposition. Washing with dilute ammonium hydroxide as recommended by Angeletti (*13*) fails to completely remove excess reagent.

The precipitate of zirconium cupferrate obtained from homogeneous solution does not suffer from these difficulties. The complex can be obtained in an extremely pure form and it need not

TABLE 1

Cupferrates

	Zirconium	Thorium
Materials	Zr, 5–50 mg/100 ml H_2SO_4, 6–10 vol. % C_6H_5NHOH, 0.7 g/20 ml water $NaNO_2$, 10 ml of 10% solution	Th, 4–70 mg/100 ml pH 1–3 C_6H_5NHOH, 1 g/20 ml water $NaNO_2$, 10 ml of 15% solution
Temperature of reaction mixture	0–5°C	0–5°C
Drying temperature of precipitate	100 ± 5°C	First dried at 60°C, then ignited at 800–900°C
Weighing form	$Zr(C_6H_5N_2O_2)_4$	ThO_2

TABLE 2

Salicylaldoximates

	Nickel	Palladium
Materials	Ni, 5–20 mg (5 ml) Alcohol, 200 ml(30%) Buffer pH 10, 25 ml Salicylaldehyde, 0.8 ml/2 ml alcohol NH_2OH, HCl, 0.5 g/10 ml	Pd, 3–50 mg/5 ml Alcohol, 200 ml(30%) H_2SO_4, 2–2.5 vol. % Salicylaldehyde, 0.5 ml/2 ml alcohol NH_2OH, HCl, 0.25 g/10 ml
Temperature of reaction mixture	Room temperature	Room temperature
Drying temperature of precipitate	120° ± 5°C	110° ± 5°C
Weighing form	$Ni(C_7H_6O_2N)_2$	$Pd(C_7H_6O_2N)_2$

require ammonia washing. Simple washing with cold water removes the excess reagents completely.

The possibility of directly weighing the precipitate as the cupferron complex offers a really great advantage in that the gravimetric factor is considerably improved [0.1428 for $Zr/Zr(C_6H_5N_2O_2)_4$ as compared to 0.7404 for Zr/ZrO_2].

The analysis of zirconium precipitate gave N, 18.01% (theoret. 17.65%), and Zr, 14.30% (theoret. 14.26%), confirming the composition $Zr(C_6H_5N_2O_2)_4$.

The thorium cupferrate complex has to be ignited because of the lack of characteristic chemical stability. The precipitate obtained from homogeneous solution needs similar ignition. An attempt to weigh the precipitate directly was not successful, so it appears that it must be ignited to the dioxide.

The cupferrates obtained from homogeneous solution are of fairly large particle size. Attempts were made to use coarse filtering media to filter the cupferrate precipitates. For this sintered glass crucible No. 3 and Whatman filter paper No. 40 were tried for zirconium and thorium cupferrate precipitates, respectively. But in both cases the precipitates passed through, yielding slightly low results. In the presence of tartaric acid—in particular, in the case of thorium cupferrate—the precipitate appeared finer in nature and caused trouble in filtering. In this case, addition of filter-paper pulp and use of Whatman filter paper No. 42 was found to be very suitable for easy filtering and subsequent ignition of the precipitate.

The method is applicable to the determinations of 5–50 mg zirconium and 4–70 mg thorium (Table 3). Larger amounts of cations

TABLE 3

Determination of Zirconium and Thorium

Taken, mg	Found, mg[a] Conventional precip.	Found, mg[a] Homogeneous precip.
Zr, 11.70	—	Zr, 11.80
Zr, 23.40	—	Zr, 23.40
Zr, 46.81	Zr, 46.98	Zr, 46.90
Zr, 58.32	Zr, 58.53	Zr, 58.40
Th, 4.03		Th, 4.10
Th, 20.15		Th, 20.31
Th, 40.30	Th, 38.91	Th, 40.35
Th, 56.42	Th, 54.06	Th, 56.40
Th, 80.60	Th, 78.10	Th, 80.65

[a] Average of three results.

are avoided because of the bulky nature of the precipitates. In both cases the determinations have been compared with those of the conventional method of precipitation by cupferron.

Nature and Composition of the Salicylaldoximates

The method is applicable to the determinations of 5 to 50 mg nickel and 3 to 50 mg palladium (Table 4). Large amounts of nickel and palladium are avoided because of the voluminous nature of the precipitates. In both cases the determinations have been compared with those of the conventional method of precipitation with salicylaldoxime. For this purpose salicylaldoxime was prepared according to the procedure of Vogel (*14*). The method is precise, more rapid, and less time-consuming than many other gravimetric methods for the determination of nickel and palladium.

TABLE 4

Determination of Nickel and Palladium

Taken, mg	Found, mg[a] Conventional precip.	Found, mg[a] Homogeneous precip.
Ni, 6.45		6.48
Ni, 12.90	12.90	12.90
Ni, 25.80	26.09	25.85
Ni, 51.60	51.90	51.70
Pd, 5.43	5.25	5.40
Pd, 10.86	10.55	10.88
Pd, 21.72	21.60	21.75
Pd, 54.30	54.38	54.32

[a] Average of three results.

Nitrogen analyses were run to establish the composition of the salicylaldoximates of nickel and palladium obtained from homogeneous solution and to prove their identity with the precipitates with salicylaldoxime. These showed good agreement with the theoretical values. Nickel salicylaldoximate gave N, 8.40% (theoret. 8.48%), and palladium salicylaldoximate gave N, 7.48% (theoret. 7.40%), confirming the compositions $Ni(C_7H_6O_2N)_2$ and $Pd(C_7H_6O_2N)_2$, respectively.

To ascertain the completeness of the precipitation of nickel and palladium by the proposed methods, the filtrates in both cases were evaporated to small volumes and tested with dimethylglyoxime, but negative results were obtained in both cases.

Thermogravimetric Behavior of the Cupferrates

From the thermolysis curve of zirconium cupferrate obtained from homogeneous solution it is found that the precipitate is quite stable up to 200°C, beyond which decomposition starts, and at 850°C and higher, dioxide is formed. The precipitate of thorium cupferrate obtained from homogeneous solution was dried in an oven with a gradual rise of temperature. It was found that at ~80°C decomposition starts, that some sticky material was subsequently formed, and that this changed into a grayish mass at ~90°C.

Thermogravimetric Behavior of Salicylaldoximates

Nickel salicylaldoximate is quite stable up to 220°C, beyond which decomposition starts; from 430°C upward the weight remains constant. Palladium salicylaldoximate, on the other hand, is stable up to 240°C, and decomposition starts between 240° and 270°C; the weight remains constant from 500°C. In both decompositions the material left had a "puffed-up" appearance.

Effect of Acidity and pH

The effect of various acid concentrations and pH on the homogeneous precipitation of zirconium and thorium cupferrates was studied. The precipitation of zirconium cupferrate starts at 0.5 vol. % sulfuric acid concentration and is completed at 6 to 10 vol. % sulfuric acid concentration. At still higher acid concentrations, sodium nitrite tends to decompose and the precipitate cannot be obtained in a weighable form.

In the case of thorium, the precipitations were carried out over the pH range 0.5 to 5. It was found that at pH 0.5, the reagent decomposes in the presence of thorium, and the pH range 1 to 3 was found suitable for complete precipitation of thorium cupferrate (Tables 5 and 6).

Precipitation of nickel salicylaldoximate starts at pH 3.1 and is complete at pH 9.0. The optimum pH range is pH 9.0 to 10.5. At

TABLE 5

Effect of Acid Concentration (Zr, 23.40 mg)

Acid concn., vol. % H_2SO_4	Zirconium found, mg
2	22.78
3	22.91
4	22.93
5	23.09
6	23.36
7	23.44
10	23.43

TABLE 6

Effect of pH (40.30 mg of Thorium)

pH (initial)	Thorium found, mg
3.1	40.38
2.5	39.80
2.0	39.90
1.5	39.85
1.0	40.10
0.5	Reagent decomposes

still higher pH, the precipitate shows slight solubility, yielding somewhat low results (Table 7).

The point of incipient precipitation of palladium salicylaldoximate is at acid concentration below 0.5 vol. % sulfuric acid and 2 to 2.5 vol. % sulfuric acid concentration was found optimum for complete precipitation of palladium salicylaldoximate (Table 8).

Reagent Concentration

The amounts of phenylhydroxylamine and sodium nitrite are not critical. In both the case of zirconium and thorium cupferrates fairly large excess of phenyl hydroxylamine and sodium nitrite are tolerable. In these cases, the excess reagents added can be removed completely by repeated washing of the cupferrates by the proposed wash solutions.

TABLE 7

Effect of pH on Nickel Salicylaldoximate (Ni, 12.90 mg)

pH (initial)	Found, mg
7.5	12.72
8.0	12.80
8.5	12.85
9.0	12.89
9.5	12.91
10.0	12.93
10.5	12.93
11.0	12.74
12.0	12.61

TABLE 8

Effect of Acid Concentration on Palladium Salicylaldoximate (Pd, 10.86 mg)

Acid concn., vol. % of H_2SO_4	Found, mg
0.5	10.68
1.0	10.69
1.5	10.76
2.0	10.84
2.5	10.83
3.0	10.94
3.5	10.92

The amounts of salicylaldehyde and hydroxylamine hydrochloride are not critical in either case. Fairly large excess of the reagents is tolerable in both the cases of nickel and palladium salicylaldoximates. In case of addition of excess reagents, the precipitates must be washed repeatedly with the proposed wash solutions to remove the excess reagents.

Effect of Wash Liquid

In the case of zirconium cupferrate, simple washing of the precipitate with cold water removes the excess reagent completely, and yields good results. Washing the precipitate with cold dilute sulfuric acid or hydrochloric acid followed by washing with cold water yields a high result, and ammonia wash was found to decompose the precipitate.

Different wash solutions were tried to wash the thorium cupferrate precipitate, but it was found that washing with cold 1:10 hydrochloric or 1:20 sulfuric acid, then with 1:10 ammonia, and finally with cold water gave quantitative results.

The precipitates of nickel and palladium salicylaldoximates must be washed carefully to remove excess reagents. For this reason, the nature of the wash solutions is very important. Different wash solutions in different volumes were tried, and it was found that 30% alcoholic solutions are best in both the cases of nickel and palladium salicylaldoximates. With warm water (60°C) as a wash solution, some tarry matter was found to form, and with dilute acid and dilute ammonia as the wash solutions for palladium and nickel salicylaldoximates, respectively, high results were obtained.

DIVERSE IONS

Zirconium

Thornton and Hayden (*15*) reported that the separation of zirconium from phosphoric acid by precipitating the former with cupferron is impossible. Later it was found that fair separations are possible if the acidity is maintained as high as 10 vol. % sulfuric acid, and the concentration of P_2O_5 does not exceed 0.02 g/400 ml of the solution. But a successful separation can be carried out by the technique of homogeneous precipitation using the following procedure.

Add 2.5 g of EDTA to a zirconium solution containing 20.64 mg of zirconium and 10 vol. % sulfuric acid. Warm the solution to 60°C. Add ammonium phosphate solution containing not more than 30 mg of phosphorus. Stir well, cool the solution, and precipitate zirconium cupferrate as usual. By this procedure up to 30 mg of phosphorus can be separated from zirconium. Copper, titanium, vanadium, and uranium(VI) and, among the anions, citrate, tartrate, fluoride, oxalate, chloride, and EDTA do not interfere (Table 9).

Thorium

In the determination of thorium, there are many interferences. But a few interfering ions can be eliminated by appropriate masking agents (Table 10).

TABLE 9

Diverse Ions (Zr, 20.64 mg)

Ions present	Added as	Tolerance limit, mg
Ti^{4+}	$Ti(SO_4)_2$	40[a]
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	50[b]
V^{5+}	$NaVO_3$	30[c]
$C_2O_4^{2-}$	Oxalic acid	1×10^2
Citrate	Citric acid	2×10^3
Tartrate	Tartaric acid	2×10^3
Cl^-	NaCl	7×10^2
EDTA	Disodium salt	2×10^3
PO_4^{3-}	$(NH_4)_3PO_4$	30[b]

[a] Masked with EDTA and F^-.
[b] Masked with EDTA.
[c] Masked with tartaric acid.

TABLE 10

Diverse Ions (40.30 mg of Thorium)

Ions present	Added as	Tolerance limit, mg
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	50[a]
Ti^{4+}	$Ti(SO_4)_2$	50[b]
V^{5+}	$NaVO_3$	25[c]
Ta^{5+}	Ta-tartrate	40
Tartrate	Tartaric acid	2×10^3
Citrate	Citric acid	2×10^3
F^-	NH_4F	2×10^3
EDTA	Disodium salt	2×10^3
PO_4^{3-}	$(NH_4)_3PO_4$	2×10^3[a]

[a] Masked with EDTA.
[b] Masked with EDTA and F^-.
[c] Masked with tartaric acid.

In the separation of vanadium from thorium, the precipitate of thorium cupferrate becomes orange-red in color. But this color may be removed by repeated washing the precipitates with wash solutions.

Nickel and Palladium

Ions that commonly occur in association with nickel and palladium were tested for interference. The results of this study are shown in Tables 11 and 12. Cobalt and manganese were tested at several levels. Amounts of cobalt and manganese in excess of 15 mg caused the formation of salicylaldoximates in the case of nickel, resulting in weights well above the theoretical value. To remove the

TABLE 11

Diverse Ions (Ni, 12.90 mg)

Ions present	Added as	Tolerance limit, mg
Tartrate	Tartaric acid	2×10^3
Oxalate	Sodium oxalate	1×10^3
F^-	NH_4F	1×10^3
Citrate	Citric acid	2×10^3
PO_4^{3-}	$(NH_4)_3PO_4$	1×10^3[a]
EDTA	Disodium salt	None
Bi^{3+}	BiOCl	2×10^2
Fe^{3+}	$Fe(NH_4)(SO_4)_2 \cdot 12H_2O$	60[b]
Mn^{2+}	$MnSO_4$	15[b]
Co^{2+}	$CoSO_4$	15[c]
Hg^{2+}	$Hg(NO_3)_2$	2×10^3[d]
Ag^+	$AgNO_3$	1×10^2

[a] Masked with citric acid.
[b] Masked with triethanolamine.
[c] Masked with thiocyanate.
[d] Masked with iodine.

TABLE 12

Diverse Ions (Pd, 10.86 mg)

Ions present	Added as	Tolerance limit, mg
Co^{2+}	$CoSO_4$	2×10^2
Ni^{2+}	$Ni(NO_3)_2 \cdot 6H_2O$	2×10^2
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	10
Fe^{3+}	$Fe(NH_4)(SO_4)_2 \cdot 12H_2O$	2×10^2
Ag^+	$AgNO_3$	1×10^2
Tartrate	Tartaric acid	2×10^3
Citrate	Citric acid	2×10^3
Oxalate	Sodium oxalate	1×10^3
F^-	NH_4F	1×10^3
PO_4^{3-}	$(NH_4)_3PO_4$	1×10^3

interference of silver, hydroxylamine hydrochloride was converted to hydroxylamine sulfate by fuming with concentrated sulfuric acid. For this purpose, a known amount of palladium chloride was converted to palladium sulfate, dissolved in a known volume of water, and estimated with dimethylglyoxime.

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