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ABSTRACT

Barium may be determined gravimetrically in hydrated zirconyl chloride and in zirconium metal. Since zirconium interferes in the precipitation of barium as barium sulfate, a method is described for the complete separation of the zirconium (and iron) before the final determination of the barium.

The bulk of the zirconium is removed by two filtrations at controlled acidities; a cupferron precipitation-chloroform extraction separates any residual zirconium.

Gravimetric studies made for the precipitation of barium ranging from 0.2 to 2.0 mg indicated that best results are obtained by the addition of a large excess of ammonium sulfate.

I. INTRODUCTION

Because of its favorable nuclear properties and high resistance to corrosion by sodium, zirconium has been favored as the structural material in sodium-cooled high temperature atomic energy reactors.

Barium was first qualitatively detected in zirconium metal by spectrographic means. Possibly, any barium present in zirconium may be leached from the structural metal when immersed in hot sodium, and thus accelerate the destruction of the zirconium metal. Therefore, a study was undertaken to develop a reliable wet method for the determination of microgram-quantities of barium in zirconium; in this manner the specific effect of hot sodium on zirconium metal could be ascertained.

However, before barium could be determined, a means for a preliminary separation of the zirconium had to be developed, because attempts to determine barium in the presence of zirconium produced high results. No specific information has been published on the bulk separation of large amounts of zirconium, and only general knowledge was cited.[1] The precipitation of zirconyl chloride as a method for the purification of zirconium was suggested[1,2] without the necessary details of the solubility of zirconyl chloride.[2,3]

Studies were undertaken to determine the conditions of the optimum insolubility range of zirconyl chloride in hydrochloric and hydrofluoric acid solutions. A schematic for this separation of zirconium might then be applied as a general separation for determining other impurities in zirconium.

A gravimetric method for the determination of barium was preferred in order that all precipitates could be checked by X-ray fluorescence for zirconium and other impurities.

Caley and Moore[4] offered no details on determining barium gravimetrically using ethyl methyl picrate as a precipitating reagent, and more developmental work would have been required to determine 0.2 mg of barium gravimetrically.

The methods used most frequently for the gravimetric determination of barium are the sulfate and the chromate procedures.[5] The rhodizonate[6] and the 8-quinolinol[5] methods were too insensitive in the lower concentration ranges. The barium sulfate procedure was selected.

Deal[7] precipitated barium with sulfuric acid in 1:1 hydrochloric acid solution (pH about 0.2). Deal's results were just slightly high in the 0.5 to 2.5 mg range and no data were given for smaller quantities of barium.

A schematic for the separation of barium and zirconium metal is shown in Fig. 1.

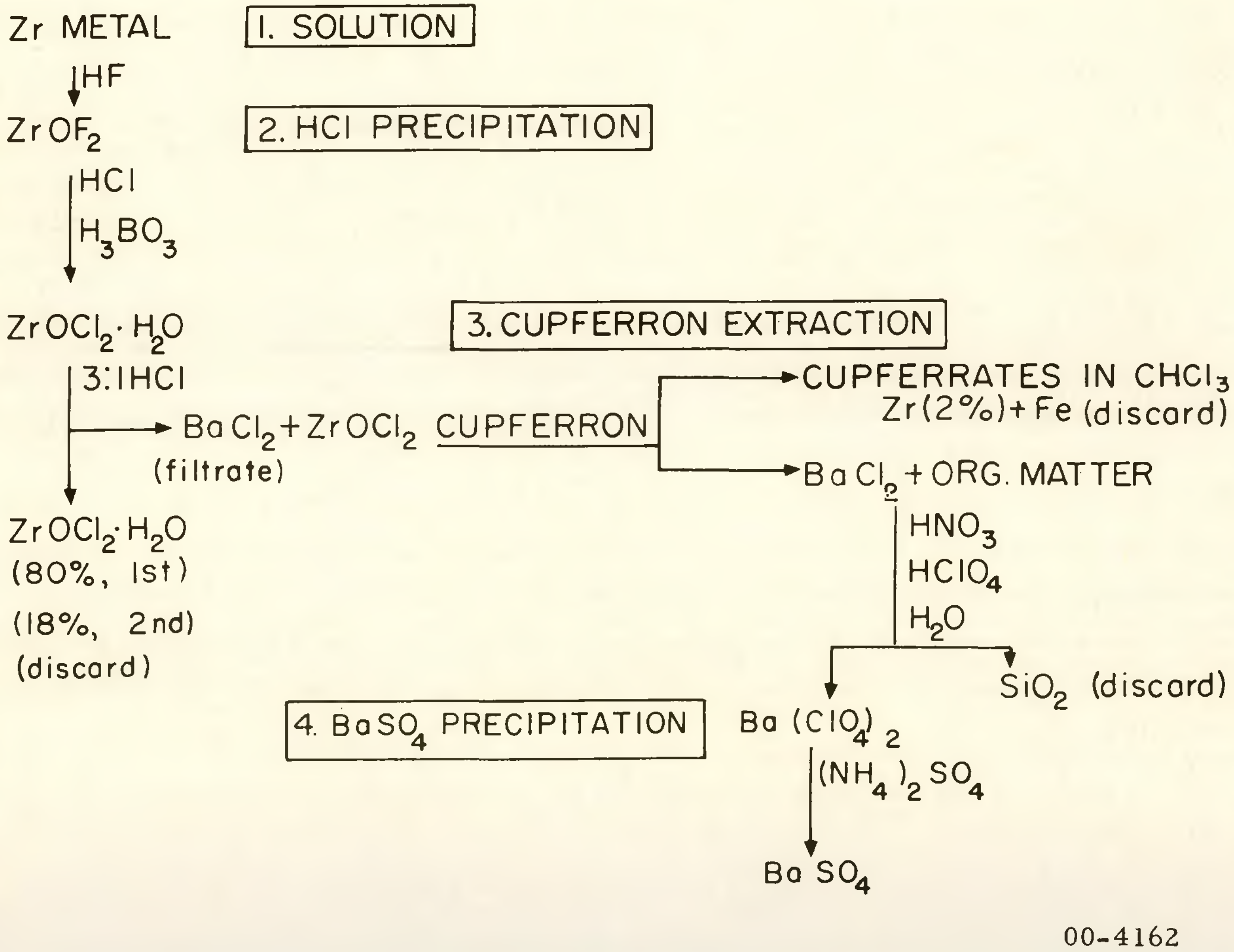

Fig. 1 Schematic for Separation of Barium from Zirconium Metal

II. PROCEDURE

A. HYDRATED ZIRCONYL CHLORIDE

Dissolve 30 grams of zirconyl chloride (30 g $ZrOCl_2 \cdot 8H_2O \equiv 8.5$ g Zr) with a minimum amount of water (30 to 35 ml) in a 150-ml beaker. Add twice the calculated theoretical amount of hydrochloric acid (40 ml) to precipitate the zirconium as zirconyl chloride. Evaporate with caution to about 5 ml over an asbestos gauze. Adjust the acidity to 3:1 hydrochloric acid and the total volume to 20 ml by the addition of 2.5 ml of water and 12.5 ml of concentrated hydrochloric acid. Cool in an ice bath. Filter through a 125-ml "medium" sintered glass funnel using suction. Wash with a minimum amount of cold 3:1 hydrochloric acid. (The residue may be dried at 55° C and then be considered purified zirconyl chloride.) Transfer the filtrate to a 150-ml beaker with water, and evaporate to a small volume (approximately 5 ml). Add 5.0 ml of concentrated hydrochloric acid. The solution is now 3:1 hydrochloric acid in a total volume of 10 ml. Cool slightly in an ice bath. Filter through a 60-ml "medium" sintered glass funnel. Wash with a minimum of cold 3:1 hydrochloric acid. Transfer the filtrate to a 500-ml separatory funnel with water. Make the solution 10 per cent in hydrochloric acid by the addition of 15 ml of hydrochloric acid, 75 ml of water, and 100 ml of aqueous 6 per cent cupferron solution. Mix. Add 100 ml of chloroform and shake for 2 to 3 minutes. Allow to separate; drain off the lower chloroform layer and discard. (If the previous precipitate was heavy, perform an additional extraction: add 5 ml of concentrated hydrochloric acid, 50 ml of 6 per cent cupferron solution and 100 ml of chloroform; shake 2 to 3 minutes and discard the lower chloroform layer.) One extraction is usually sufficient. A green color in the water solution indicates decomposition products of cupferron. Add 100 ml of chloroform; shake and discard the final organic layer. Transfer the virtually zirconium-free, iron-free filtrate to a 600-ml beaker and evaporate to half-volume. Add 100 ml of nitric acid and evaporate to half-volume again. Add 25 ml more of nitric acid and 15 ml of perchloric acid. Fume to near-dryness. Cool. Add 50 ml of water, boil gently for 5 minutes and filter into a 600-ml beaker. Wash with hot 2 per cent hydrochloric acid. Discard the residue. Dilute the filtrate to 150 ml. Neutralize with 1:1 ammonium hydroxide; adjust the pH to 0.65 with 1:1 hydrochloric acid. Heat to boiling and add 15 ml of a fresh 50 per cent ammonium sulfate solution dropwise with stirring. Mark the volume with a marking pencil. Boil gently 15 to 20 minutes, adjust the volume to the mark and add 15 ml more of 50 per cent ammonium sulfate. Boil gently until fine barium sulfate crystals coagulate and settle. Maintain the original volume by the addition of water. Allow the sample to stand overnight, if possible. Filter by decantation through a No. 42 Whatman filter paper using paper pulp. Transfer the final residue to the filter paper. Wash with hot water containing 1 per cent ammonium sulfate and 0.1 per cent sulfuric acid. Transfer the paper containing barium sulfate to a porcelain crucible. Dry, char, ignite at 850° C overnight and weigh. Calculate per cent barium.

B. ZIRCONIUM METAL

Weigh a 10-gram sample of zirconium metal chips and place in a large platinum evaporating dish. Add enough water (approximately 10 ml) to completely immerse the metal. Add a total of 25 ml of hydrofluoric acid dropwise from a small polyethylene bottle with an occasional addition of several milliliters of water to prevent crystal formation. Heat to evolve excess hydrofluoric acid; evaporate to incipient crystallization. Add twice the theoretical amount of concentrated hydrochloric acid to precipitate the zirconium as zirconyl chloride. (About 40 ml of concentrated hydrochloric acid are required per 10 grams of zirconium metal.) Calculate the theoretical amount of boric acid necessary to combine with the hydrofluoric acid. (Approximately 12 grams of boric acid are required per 25 ml of hydrofluoric acid.) Add the solid boric acid to the sample and slowly evaporate the entire sample to a small volume. Evaporate over an asbestos gauze to prevent bumping. Wash down the sides with a small amount of water and continue evaporating to a volume of approximately 5 ml. Add 2.5 ml of water plus 12.5 ml of concentrated hydrochloric acid, making the total volume 20 ml of 3:1 hydrochloric acid solution. Proceed as under hydrated zirconyl chloride.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. BULK SEPARATION OF ZIRCONYL CHLORIDE

Zirconyl chloride octa-hydrate crystals dissolve readily in water, but are slightly less soluble in concentrated hydrochloric acid. In order to re-precipitate the dissolved zirconium, the addition of concentrated hydrochloric acid, in a limited volume, seemed most logical.

A series of solubility tests were made (Table I) in which 5 grams of zirconyl chloride (≡ 1.42 g Zr) were dissolved in selected concentrations of hydrochloric acid in order to find the optimum point of insolubility. Optimum insolubility occurred in a 3:1 hydrochloric acid medium, where only 0.14 to 0.20 gram zirconium remained in solution. As much as 1.3 grams (86 per cent of the zirconium) were removed by filtration. In No. 9, Table I, only 0.10 gram zirconium remained in solution, but the total volume used here was only 10 ml. A 10-ml volume may be slightly inconvenient if a 10-gram starting sample of zirconium is used.

TABLE I

SOLUBILITY OF ZIRCONIUM

$ZrOCl_2 \cdot 8H_2O$ used: 5.0 g (1.42 g Zr)					Zr (g)	
No.	HCl (ml)	H_2O (ml)	$HCl:H_2O$	Total Volume	Soluble	Insoluble
1.	0	30	0:30	30	1.42	none
2.	10	20	1:2	30	1.42	none
3.	15	15	1:1	30	0.39	1.03
4.	15	15	1:1	30	0.33	1.09
5.	20	10	2:1	30	0.21	1.21
6.	22.5	7.5	3:1	30	0.20	1.22
7.	22.5	7.5	3:1	30	0.14	1.28
8.	30	0	30:0	30	0.67	0.75
*9.**	*5*	*5*	*1:1*	*10*	*0.18*	*1.32*

*Volume of only 10 ml total.

Experimental results showed that 80 per cent of the zirconium was separated by filtration (Table II). X-ray diffraction patterns indicated that a fairly pure hydrated zirconyl chloride was removed in this first separation. Chemical analysis of the precipitate approximated a quinque-hydrate.[2] The second filtration removed all but about 0.25 gram of the zirconium salt. X-ray diffraction patterns of this separated salt indicated the formation of still another hydrated zirconyl chloride and chemical analysis showed 11 to 12 molecules of water.

TABLE II

REMOVAL OF BULK OF ZIRCONIUM AS ZIRCONYL CHLORIDE

No.	Zr Used (g)	HCl:H_2O	Zr Removed 1st Separation (g)	(%)
1.	10.0	~1:1	3.7	37
2.	10.0	~1:1	4.1	41
3.	10.0	>1:1	8.0	80
4.	10.0	3:1	8.4	84
5.	10.0	3:1	8.1	81
6.	10.0	3:1	8.0	80
7.	10.0	3:1	8.0	80

The residual zirconium and any interfering quantities of iron were precipitated with cupferron and extracted and removed with chloroform.[8] In order to insure complete separation of the zirconium, the acidity was adjusted to 10 per cent hydrochloric acid before the cupferron extraction and quantities of 6 grams or of 6 and 3 grams of cupferron in solution respectively were added. A determination of zirconium in the filtrate[9] indicated that a residual of 10 micrograms or less may be expected. The final filtrate was virtually iron-free and zirconium-free.[8]

After fuming with nitric and perchloric acids, a rapid filtration removed any silica.

B. PRECIPITATION OF BARIUM AS BARIUM SULFATE

Preliminary studies were made in water solution to determine the optimum conditions for the gravimetric determination of barium.

From a series of synthetic solutions in which the barium concentration was varied from 0.5 to 3.0 mg, extremely high results were obtained when sodium sulfate was used as a precipitating agent. The differences in recoveries ranged from 2.9 to 7.2 mg, an indication of coprecipitation of the sodium salts. When small volumes of 1:1 sulfuric acid solution were added in a similar series (final pH 0.7 to 0.8), Table III, the results were slightly low; as much as -0.3 mg loss in barium was noted in the 2.0 mg synthetic solution. When the added volume of 1:1 sulfuric acid solution was increased to 10 ml, no improvement in the recovery of the barium (Table III) was noted. Results were still low.

TABLE III

DETERMINATION OF BARIUM IN WATER SOLUTION

Precipitating Agent- 1:1 H_2SO_4

No.	1:1 H_2SO_4 (ml)	Final Filtrate (pH)	Ba Added (mg)	Ba Found (mg)	Difference (mg)
1.	2.0	----	0.0	0.0	0.0
			0.5	0.6	+0.1
			1.0	0.9	-0.1
			2.0	1.7	-0.3
2.	3.0	0.7-0.8	0.0	0.0	0.0
			1.0	0.8	-0.2
			2.0	1.7	-0.3
3.	10.0	0.2-0.3	0.0	0.0	0.0
			0.0	0.0	0.0
			0.5	0.3	-0.2
			0.5	0.3	-0.2
			1.0	0.9	-0.1
			1.0	0.9	-0.1
			2.0	1.7	-0.3
			2.0	1.7	-0.3

Further study indicated that when a sufficiently large amount of ammonium sulfate was used as precipitating reagent for barium, complete recovery of the barium resulted. 5-gram and 10-gram portions of ammonium sulfate (Table IV, No. 1, 2, and 3) proved inadequate.[10] The variation of solution pH from 0.0 and 1.4 produced no significant differences, except, that when a pH just above one was maintained (Table IV, No. 4), a tendency toward more complete recovery of the barium was noted.

TABLE IV

DETERMINATION OF BARIUM IN WATER SOLUTION

Precipitating Agent-50% $(NH_4)_2SO_4$

No.	$(NH_4)_2SO_4$ (g)	Final Filtrate (pH)	Ba Added (mg)	Ba Found (mg)	Difference (mg)
1.	5.0	0.9-1.0	0.0	0.0	0.0
			0.5	0.4	-0.1
			1.0	1.1	+0.1
			2.0	1.7	-0.3
2.	5.0	0.3-0.4	0.0	0.0	0.0
			1.0	0.7	-0.3
			2.0	1.8	-0.2
3.	10.0	0.0-0.4	0.0	0.0	0.0
			0.5	0.4	-0.1
			1.0	0.9	-0.1
			2.0	1.8	-0.2
4.	10.0	1.0-1.4	0.0	0.0	0.0
			0.0	0.0	0.0
			0.5	0.4	-0.1
			0.5	0.4	-0.1
			1.0	0.8	-0.2
			1.0	0.9	-0.1
			2.0	1.8	-0.2
			2.0	1.9	-0.1

TABLE IV (Continued)

DETERMINATION OF BARIUM IN WATER SOLUTION

Precipitating Agent-50% $(NH_4)_2SO_4$

No.	$(NH_4)_2SO_4$ (g)	Final Filtrate (pH)	Ba Added (mg)	Ba Found (mg)	Difference (mg)
5.	15.0*	1.1-1.3	0.0	0.0	0.0
			0.0	0.0	0.0
			0.0	0.0	0.0
			0.0	0.1	+0.1
			0.2	0.2	0.0
			0.2	0.3	+0.1
			0.5	0.5	0.0
			0.5	0.5	0.0
			0.5	0.6	+0.1
			0.5	0.6	+0.1
			1.0	1.0	0.0
			1.0	1.0	0.0
			1.0	1.1	+0.1
			2.0	2.0	0.0
			2.0	2.1	+0.1

*$(NH_4)_2SO_4$ - added in two 15-ml portions.

When the amount of ammonium sulfate precipitant was increased to 15 grams (Table IV, No. 5) in a slightly acid medium (pH 1.0), very satisfactory recovery of milligram-quantities of barium resulted. By adjusting the pH of the prepared (zirconium-free, iron-free) solution to 0.65 and by maintaining the same volume after the addition of ammonium sulfate, a pH of about 1.0 would be maintained. The addition of ammonium sulfate in two separate portions together with gentle boiling formed an easily-filterable barium sulfate.

C. DETERMINATION OF BARIUM IN ZIRCONYL CHLORIDE

In a series of samples, zirconyl chloride was varied from 0 to 30 grams and the sample analyzed for barium. Impure zirconyl chloride crystals contained an average of 0.056 per cent barium (Table V, No. 1 to 4).

TABLE V

DETERMINATION OF BARIUM IN ZIRCONYL CHLORIDE

No.	Source	$ZrOCl_2$ Used (g)	Ba Added (mg)	Ba Found (mg)	Ba Found (%)	Deviation from the Mean
1.	Blank	0.0	0.0	0.1		
2.	Impure	5.0	0.0	0.9	0.066	+0.010
3.	Impure	15.0	0.0	2.3	0.054	-0.002
4.	Impure	30.0	0.0	4.0	0.047	-0.009
5.	Purified	30.0	0.0	1.5	0.017	+0.001
6.	Purified	30.0	0.0	1.3	0.015	-0.001
7.	Purified	30.0	0.0	1.4	0.016	0.000
8.	Purified	30.0	0.0	1.2	0.015	-0.001
9.	Purified	30.0	0.0	1.3	0.016	0.000
						Difference (mg)
10.	1st Separation of a "Purified"	24.0	0.0	0.1	0.001	+0.1
11.	1st Separation of a "Purified"	24.0	0.2	0.3	0.003	+0.1
12.	1st Separation of a "Purified"	24.0	1.00	1.0	0.013	0.0

In a second series of samples, using purchased "purified" zirconyl chloride, five 30-gram samples of the "as received" material were analyzed for barium. This purchased purified-grade zirconyl chloride contained 0.016 per cent barium (Table V, No. 5 to 9). To 30-gram zirconyl chloride portions, recovered as residue in this analytical procedure, were added 0, 0.2, and 1.0 mg of barium respectively. Table V, (No. 10 to 12) shows that 0.1, 0.3, and 1.0 mg of barium were recovered. This is evidence that the zirconyl chloride residues are free of barium.

D. DETERMINATION OF BARIUM IN ZIRCONIUM METAL

Available samples of zirconium metal were also analyzed for barium (Table VI). Crystal bar zirconium contained 0.000 and 0.001 per cent barium, structural zirconium metal sheet contained 0.003 and 0.004 per cent barium, and zirconium tubing contained 0.001 per cent.

TABLE VI

DETERMINATION OF BARIUM IN ZIRCONIUM METAL

No.	Type Zr	Zr Metal (g)	Ba Added (mg)	Ba Found (mg)	Ba (%)
1.	Cyrstal Bar	10.00	0.0	0.0	0.000
2.	Crystal Bar	10.00	0.0	0.1	0.001
3.	Tubing	10.00	0.0	0.1	0.001
4.	Sheet	10.14	0.0	0.4	0.004
5.	Sheet	10.12	0.0	0.3	0.003
5a.	Sheet	10.14	1.0	1.3	0.013

When a known amount of barium was added to the structural sheet, barium was recovered ±0.001 per cent (Table VI, No. 5a).

X-ray fluorescence analysis of the final barium sulfate residue showed complete separation of the zirconium, and absence of other impurities.

IV. SUMMARY

Barium may be determined gravimetrically in quantities ranging from 0.2 to 2.0 mg (±0.1 mg) in hydrated zirconyl chloride and in zirconium metal after complete separation of the zirconium. As much as 10 grams of zirconium may be removed by a double precipitation in a 3:1 hydrochloric acid medium followed by a cupferron precipitation-chloroform extraction of the residual zirconium.

The barium is then determined gravimetrically as barium sulfate in the iron-free, zirconium-free filtrate by precipitation with an excess of ammonium sulfate.

As much as 0.056 per cent barium has been found in impure zirconyl chloride, 0.016 per cent in "purified" zirconyl chloride, 0.000 per cent barium in crystal bar zirconium metal, and 0.003 per cent barium in zirconium metal sheet. Reproducibility is 0.001 per cent.

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