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CHELATE PROCESS FOR ISOLATING ZIRCONIUM

By

T.T. Runion

LABORATORY RECORDS
1954

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CHELATE PROCESS FOR ISOLATING ZIRCONIUM

By T. C. Runion

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1.0 Abstract

A process is presented for the isolation of radioactive zirconium from solutions of plutonium, uranium and fission products based on extraction with thenoyltrifluoroacetone (TTA) in benzene.

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2.0 Introduction

Thenoyltrifluoroacetone* (known throughout this study as TTA) is one of a series of chelating compounds developed by J. Reid, M. Calvin and co-workers at the University of California laboratories. The reaction of TTA with various metals is as follows:

$$Me^{n} + nHKe \rightleftharpoons MeKe_{n} \quad nH^{+}$$

where Me refers to a metal of valence state n and HKe refers to the acidic enol form of the TTA molecule. The mechanism of the reaction is a combination of hydrogen replacement and coordinate bonding. Both the chelating agent and the metal chelate have a negligible solubility in the aqueous phase and can be extracted with an organic solvent such as benzene. Other solvents, e.g., toluene and carbon tetrachloride, have also been found satisfactory. Among the first detailed investigations of the complexing action of TTA, with significant application to the isolation of a specific radioactive element, were those made by Crandall and Thomas in their chelate process for plutonium.[3,4] The physico-chemical studies made by these workers included a general classification of U, Pu, Th and the significant fission elements according to their extractability from 0.5M HNO_3 using 0.02M TTA. The list is as follows:

1. Zr^{IV}	6. Fe^{III}	11. Ce^{III}
2. Pu^{IV}	7. Cb^{V}	12. Pu^{III}
3. Np^{IV}	8. Y^{III}	13. Pu^{VI}
4. Ce^{IV}	9. UO_2^{II}	14. Sr^{II}
5. U^{IV}	10. Th^{IV}	

Separation of the various metals can be accomplished by appropriate variation of the TTA and acid concentrations.

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*

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The idea of using TTA as a complexing agent for Zr is not new, investigations having been made independently by Perlman, Connick, Zebroski and workers at the University of California, and members of the radioisotopes section of Oak Ridge National Laboratories, including A. Rupp, A. Broido and I. Whitney. The use of TTA for other separations have included processes for Pu, Pr, Ca, Sc, Ra and Ac.

In the Isotopes Development Section at Oak Ridge National Laboratory, radioactive zirconium is prepared in the following manner. Irradiated uranium slugs are dissolved in nitric acid and the dilute solution is then sent through an IR-I resin adsorption column. The zirconium, containing some plutonium, columbium, ruthenium and traces of rare earths, is subsequently eluted from the column with 0.5% oxalic acid. Because of the presence of oxalates, the chelation of zirconium with TTA is markedly inhibited in such solutions. In this report, the detailed investigation of such extraction process variables as TTA and acid concentrations, temperature and equilibration time, both in the presence and absence of oxalates is described, and a process is presented for the separation of the zirconium from the remaining impurities. It is recommended that this process be used for the preparation of all radioactive Zr shipments.

[redacted]

3.0 Summary

A chelate process utilizing thenoyltrifluoroacetone has been developed for the separation of radioactive Zr from Cb, Pu, Ru, Ce and other rare earths, and U. Essentially, the process is as follows: (1) Extraction of the zirconium from nitric acid solution at a pH of 0.3 using 0.03M thenoyltrifluoroacetone in benzene. (2) Scrubbing of the organic extract with a solution (0.5M HCl, 0.01M $NH_2OH \cdot HCl$, and 0.03M $FeCl_2$) to remove Cb and Pu. (3) Dilution of the organic extract, using benzene, to 0.007M thenoyltrifluoroacetone. (4) Stripping of the Zr with 1/4 volume of either 6.0M HNO_3, 6.0M HCl, 0.05M HF, or a mixture of 0.1M $H_2C_2O_4$ and 2.0M HNO_3.

The presence of free oxalates markedly inhibits the formation and extraction of the zirconium chelate. Boiling the solutions with excess permanganate does not completely destroy the zirconium-oxalate complex, but the subsequent addition of excess $Al(NO_3)_3$ effectively complexes the oxalate and increases the chelation of zirconium. Therefore, to extract zirconium completely from solutions containing oxalates, boil with permanganate and add excess aluminum nitrate and heat before carrying out the above TTA extraction procedure.

Two flowsheet runs were made with radioactive zirconium from Clinton sources. A Zr yield of 80.0% was obtained when oxalates were destroyed with $KMnO_4$. This yield was increased to 99% in another run made in the presence of excess aluminum. Tracer experiments indicated the chelation of less than 0.1% Ru and Cb, and negligible amounts of Ce, U, and Pu.

4.0 Chemistry of Zirconium

If zirconium always occurred in solution as the plus four ion, the chelation with TTA would obey the following reaction:

$$Zr^{++++} + 4\ HKe = ZrKe_4 + 4H^+$$

and the equilibrium constant, thermodynamically, would be expressed

$$K_{Zr} = E_{b/a}\left[\frac{H^+}{HKe}\right]^4$$

where $E_{b/a}$ is the distribution coefficient for the zirconium activity (benzene/aqueous) and HKe refers to the enol form of the TTA. However, there is sufficient evidence that the Zr^{+IV} occurs only in concentrated acid solutions, hydrolysis proceding in the following manner:

$$Zr^{+IV} \rightleftharpoons (Zr(OH)^{+III} \rightleftharpoons Zr(OH)_2^{+II} \rightleftharpoons * ZrO(OH)^+ \rightleftharpoons Zr(OH)_4 \qquad (9)$$

I. Perlman's group studied this problem using TTA to extract semi-micro quantities of Zr from $HClO_4$ solutions. From 2.0-0.4M acid, the hydrogen ion dependence was 3.6, meaning that there was 0.4 hydroxyl group per zirconium ion. At lower acidities hydroxyl groups appeared to be increasing to two or three. In these experiments $NaClO_4$ was used to maintain constant ionic strength while varying the hydrogen ion concentration. The TTA dependence at 2.0M hydrogen ion was also found to be approximately fourth power.[5] A closer examination of the hydrolysis and complex formation of zirconium is underway at the present time by R. E. Connick and co-workers at the University of California laboratories.[10]

The oxides of zirconium are practically insoluble in any acid, requiring fusion with such agents as $KHSO_4$ for solution. This, together with the fact that Zr hydrolyses in dilute acid solutions resulting in the plating out of insoluble colloidal activity, makes the previous history of the zirconium very important in tracer experiments.

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*No literature reference to $Zr(OH)_3$ was found.

[redacted]

5.0 Investigation of Process Variable

The investigation of the effect of hydrogen ion, TTA concentrations and agitation time were conducted with the viewpoint of establishing the optimum process conditions. The length of agitation time designated does not represent complete equilibrium, although this variable was studied through a 24-hour period. No effort was made to maintain ionic strength in studying the effect of hydrogen ion, this effect having been rather well established by Connick, Zebroski and Perlman. These data have little physical chemical significance.

5.1 Effect of Hydrogen Ion, TTA Concentration, and Equilibration Time on the Chelation of Zirconium

The effect of hydrogen ion concentration on the formation of the zirconium chelate was found difficult to determine in dilute acid solutions because of the formation of colloidal zirconium activity in solutions containing less than 0.3M hydrogen ion. As much as 50% of the activity frequently plated out on the walls of containers or on the stirrer used to mix the phases. With macro quantities (10^{-4}M) of zirconyl nitrate in dilute acid solutions the formation of colloidal zirconium could be observed by the Tyndall effect, and by low material balances when both phases were analyzed colorimetrically. Table 5.1-1 shows that the formation of the chelate decreases rapidly as the hydrogen ion concentration is increased above 0.5 molar. This point was selected as the optimum acid concentration for the extraction of the zirconium chelate.

Zirconium was found to chelate readily at any TTA concentration above 0.01M (See Table 5.1-2). At 0.03M TTA approximately 99% of the zirconium, with only traces of the contaminating elements, was extracted. Two significant factors influenced the selection of the optimum TTA concentration (0.03M) to be used: (1) the maximum zirconium with minimum extraction of contaminating elements and (2) the degree of dilution of the TTA that must be made in the final stripping

step to make possible the recovery of the zirconium from the TTA-benzene. It was subsequently found that the zirconium could be re-extracted from 0.007M TTA-benzene which indicated a dilution of a factor of three at 0.03M TTA.

The effect of stirring time is indicated in Table 5.1-3. These data show that equilibrium is reached essentially within one hour, with little additional chelation (from a process point of view) occurring after 40 minutes.

Table 5.1-1

Effect of HNO_3 Concentration on Zr Chelation

Aqueous Phase: Zr Activity in HNO_3
Organic Phase: Equal vol. 0.03M TTA-benzene
Equilibrium time: 30 min.
Temp. 25°C. ± 1°

Run No.	HNO_3 Conc. (M)	Rel. Zr. Conc.* at Equilibrium Org. (Mv.)	Aq. (Mv.)	Zr. Distribution Coefficient (Org./Aq.)	Remarks
1	0.59	93	15	6.2	No evidence of colloidal activity
2	1.0	83	36	2.3	"
3	2.07	70	37	1.9	"

*Readings determined from 5 ml. solution on gamma solution counter.

[redacted]

Table 5.1-2

Effect of TTA Concentration on Zr Chelation

Aqueous Phase: 1.0M HNO_3, purified Zr tracer

Organic Phase: Equal-vol. TTA-Benzene
Agitation Time - 20 min.

Run No.	TTA Conc. (M)	Rel. Zr Conc.* at Equilibrium Org. (Mv.)	Aq. (Mv.)	Zirconium Distribution Coefficient (Org./Aq.)
1	0.005	8.0	75.0	0.11
2	0.01	26.0	62.0	0.42
3	0.03	83.0	5.0	16.5
4	0.05	80.0	5.0	16.0
5	0.5	79.0	9.0	9.0

*Readings taken on gamma counter given in Mv. and Zr Activity for 5 ml of solution.

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Table 5.1-3

Effect of Equilibration Time on Zirconium Chelation

Aqueous Feed: HNO_3, Zr Tracer
Solvent: Equal volume 0.03M TTA-Benzene

Run No.	Stirring Time (M)	Equilibrium pH	Zr. Dist. Coeff. Org./Aq.	Initial Acidity	T°C
1	60	0.18	1.27	0.5N HNO_3	
2	60	0.25	11.58	0.5N HNO_3	
3	20	0.35	0.72	0.35N HNO_3	27°C
-	40	-	1.93	-	
-	60	-	12.53	-	
-	80	-	6.10	-	
-	100	-	9.10	-	
-	120	-	12.04	-	
4	20	0.4	5.45	0.5M HNO_3	32°C
-	40	-	4.11	-	
-	60	-	2.34	-	
5	20	0.4	3.83	0.5M HCl	32°C
-	40	-	4.18	-	
-	60	-	4.14	0.5N HCl	29.5°
6	20	0.4	3.00	-	29.5°
-	40	-	4.03	-	
7	20	0.4	0.79	0.5N HCl	29.5°
-	40	-	3.11	-	

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5.2 Removal of Pu and Cb in Scrub Step

The chelation chemistry of plutonium was thoroughly investigated by Crandall and Thomas.[3] The results of their work showed that essentially all of the plutonium extracted could be removed from the organic extract by scrubbing with a solution that is 0.01M $NH_2OH \cdot HCl$, 0.003M $FeCl_2$ and 0.5M HCl. The $FeCl_2$ reduces the Pu^{IV} (the only valence state appreciably extracted from 0.5M acid, 0.03M TTA) to Pu^{III} which is readily stripped with 0.5M acid. A recheck of these conditions was made, using Pu tracer, with the elimination of greater than 99.0% of the Pu.

5.3 Stripping of Zr-Chelate from TTA-Benzene

Stripping experiments (See Table 5.3-1) indicate that the Zr chelate could be broken and the zirconium re-extracted from 0.1M TTA using fairly concentrated acids. With 6.0M HNO_3, recovery in this step was approximately 99.0%.

Additional studies indicated that Zr could be re-extracted at higher TTA concentration if complexing agents such as HF or $H_2C_2O_4$ were used.

[redacted]

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Table 5.3-1

Stripping of Zr Chelate from TTA-Benezene

Organic Phase: Zr chelate in benzene
Aqueous Phase: Equal volume acid
Stripping Time: 20 minutes

TTA Conc. (m/l)	Stripping Medium	Dist. Coeff. Org./Aq.
0.001	H_2O	81.0
0.001	1M HNO_3	0.04
0.01	2.0M HNO_3	0.03
0.01	6.0M HNO_3	0.05
0.01	9.6M HNO_3	0.006
0.01	0.1M $H_2C_2O_4$ and 2.0M HNO_3	0.01
0.03	H_2O	248.6
0.03	0.1M HCl	118.65
0.03	0.5M HCl	133.08
0.03	1.0M HCl	106.8
0.03	6.0M HCl	
0.03	0.03M $H_2C_2O_4$	4.2
0.03	0.1M $H_2C_2O_4$	1.1
0.03	0.5M HF	0.09
1.0	H_2O	170.0
1.0	0.5M HNO_3	182
1.0	1.0M HNO_3	60.4
1.0	3.0M HNO_3	48.6
1.0	8.0M HNO_3	50.0
1.0	0.01M HNO_3	11.5

[redacted]

5.4 Chelation of Zirconium from Oxalate Solution

The presence of oxalates in the Zr tracer markedly inhibited the extraction of Zr. The presence of 10^{-4}M oxalate reduced the chelation of Zr by a factor of ca. 100. In one series of experiments three extractions were conducted with TTA benzene in which (1) oxalates were absent, (2) the feed was made 0.03M in oxalic acid and (3) 0.03M oxalic acid was added and then destroyed by boiling the solution with $KMnO_4$. All three feeds were then extracted at a pH of 0.0 using 0.03M TTA. The respective distribution coefficients were 2.29, 0.006 and 1.37.

5.41 Variation of Chelate Formation with Hydrogen Ion and TTA Concentrations, Temperature, and Equilibration Time in Oxalate Solutions.

Aside from the generally low distribution coefficients obtained in the presence of oxalates, the most significant indication is the effect of increasing hydrogen ion. Distribution coefficients using 0.5M TTA varied from 0.4 at 1.0M HNO_3 to greater than 20.00 at 8.0M acid (see Table 5.4-1). The effect of temperature in the range of 10°-40°C was not appreciable, being less than a factor of 4. (See Table 5.4-3). Scouting experiments on the effect of equilibration time indicated that zirconium chelation increased almost linearly for at least one hour. Complete equilibrium would probably be obtained at the end of much longer stirring times due to the slow breakdown of the oxalate complex in strong acids (See Table 5.4-4).

[redacted]

[redacted]

Table 5.4-1

Effect of Hydrogen Ion on Zirconium Chelation from Oxalate Solutions

Aqueous Phase: Zr tracer in 0.5N HNO_3
Solvent: Equal volume 0.5M TTA Benzene
Equilibration Time: 10 Minutes
Temperature: 28°C

Run No.	pH of Aqueous Phase	Zr Activity Extracted MV/5ml*	App. Zr. Dist. Coeff. Org./Aq.
1	0.04	116	2.0
2	0.07	102	1.56
3	0.30	84	1.04
4	0.46	82	1.12
5	0.67	48	0.52
6	1.10	30	0.30
7	2.19	6	0.058
8	3.90	12	0.128
9	5.45	16	0.190
1-A**	0.0 N**	43	0.48
3-A**	2.0 N**	104	1.66
5-A**	8.0 N**	232	38.66

* Activity determined by 5ml. of extract on gamma solution counter.

** HNO_3 - Conc. moles/liter.

[redacted]

Table 5.4-2

Effect of TTA Concentrations on Zirconium Chelation from Oxalate Solutions

Aqueous Feed: Zr tracer in 0.5N HNO_3, pH=0.65
Solvent: Equal volume TTA Benzene
Equilibration Time: 20 Minutes
Temperature: 27°C

Run No.	TTA Conc. Moles/Liter	Zirconium Activity Extracted Mv/5ml*	App. Zr Dist. Coeff. Org./Aq.
1	0.01	6	0.050
2	0.02	2	0.016
3	0.05	11	0.096
4	0.10	26	0.24
5	0.20	72	0.84
6	0.50	106	1.50
7	1.00	114	1.78
8	3.00	119	1.90

* Activity determined by measuring 5ml. of extract on gamma solution counter.

[redacted]

[redacted]

Table 5.4-3

Effect of Temperature on Zirconium Chelation from Oxalate Solutions

Aqueous Feed: Zr tracer in 0.5N HNO_3, pH 0.65
Solvent: Equal volume 0.5M TTA-Benzene
Equilibration Time: 5 Minutes

Run No.	Temperature Degrees C.	Zirconium Activity Extracted Mv/5 ml*	Zr. Dist. Coeff. Org./Aq.
1	10	40	0.40
2	20	59	0.64
3	30	82	1.00
4	40	103	1.52

* Activity determined by measuring 5ml. of extract on gamma solution counter.

[redacted]

Table 5.4-4

Effect of Equilibration Time on Zirconium Chelation from Oxalate Solutions

Aqueous Feed: Zr tracer in 0.5N HNO_3
Solvent: Equal volume of 0.5M TTA Benzene
Temperature: 27°C

Run No. * **	Equil. Time (minutes)	Zirconium Activity Extracted Organic Mv/5ml***	App. Zr. Dist. Coeff. Org./Aq.
1-A	1/2	2	0.018
1-B	1/2	5	0.046
2-A	3	3	0.026
2-B	1	6	0.058
3-A	2	4	0.036
3-B	2	8	0.072
4-A	3	5	0.046
4-B	3	17	0.170
5-A	5	9	0.084
5-B	5	25	0.26
6-A	10	21	0.20
6-B	10	38	0.42
7-A	15	22	0.22
7-B	15	46	0.52
8-A	20	30	0.30
8-B	20	56	0.70
9-A	30	42	0.46
9-B	30	70	0.92
10-A	40	46	0.54
10-B	40	88	1.36
11-A	50	72	0.92
11-B	50	96	1.64
12-A	60	118	1.56
12-B	60	128	2.06

*pH=3.45 for A

**pH=2.00 for B

***Activity determined by measuring 5 ml. of extract on gamma solution counter.

5.42 Destruction of Oxalates with Potassium Permanganate

It was shown in section 5.4 that oxalates had a marked inhibiting effect on the chelation of zirconium. The addition of permanganate to hot zirconium oxalate solutions apparently destroyed the oxalic acid. It was necessary, however, to heat the solutions for one hour with a two-fold excess of permanganate and 0.5M nitric acid to get rid of the zirconium oxalate complex.

5.43 Improvement of Zirconium Chelation by Addition of Excess Aluminum Nitrate

The treatment of zirconium in oxalic acid-oxalate solutions with permanganate apparently destroyed most of the free oxalates but there was evidence that residual traces of a zirconium-oxalate complex still existed. It was found that chelation of zirconium took place more rapidly after the addition of excess Th or Al ions, to complex the residual oxalate. Since traces of Th react with TTA under the extraction conditions it was decided to use aluminum. It was found possible to increase zirconium chelation by a factor of 10 even in the presence of 0.5% oxalic acid when a 1.0M excess of $Al(NO_3)_3$ was added to the solution (see Table 5.4-5). Spectrographic analyses indicated no aluminum chelation under the process conditions.

Table 5.4-5 [redacted]

Effect of $Al(NO_3)_3$ on Chelation of Zr from Solutions Containing Oxalates

Aqueous Feed: Zr-Oxalate Tracer, HNO_3

Organic Phase: Equal volume TTA-Benzene

Run No.	pH	Oxalic Acid Concentration (m/l)	$Al(NO_3)_3$ Concentration	TTA Concentration (m/l)	Zr Dist. Coefficient Org./Aq.
1.0	0.65	10^{-4}	0.0	0.02	0.004
2.0	0.1	$2x10^{-4}$	0.0	0.03	0.12
3.0	1.8	$2x10^{-4}$	1.0	0.03	1.42
4.0	0.1	$2x10^{-4}$	1.0	0.03	2.02
5.0	0.1	$2x10^{-4}$	1.0	0.05	3.13
6.0	0.1	0.055M (0.5%)	1.0	0.05	1.3
7.0	0.1	0.055M (0.5%)	1.0	0.03	1.2
8.0	0.1	0.055M (0.5%)	1.0	0.03	0.54
9.0	0.1	0.055M (0.5%)	0.25	0.03	0.15

[redacted]

5.5 Chelation of Cb, Ce, Ru, Al, Th, U, and Pu under Conditions of Optimum Zr Extraction

Cb, Ce and Ru tracers in 0.5M HNO_3 were extracted with 0.03M TTA in benzene. Results indicated that the extraction coefficient for Zr was approximately a factor of 1000 higher than that for each of these elements under these conditions (see Table 5.5-1). The oxidation state of the Ce tracer used was in doubt but additional work with this element gave little evidence of greater extraction of Ce^{IV} than for Ce^{III}.

The extraction of uranium and thorium has been investigated in detail by D. C. Overholt.[11] No uranium extraction of either element occurred under the conditions observed for maximum zirconium chelation. Overholt has found that the optimum conditions for uranium chelation are at a pH of 2.0-2.3 with TTA concentrations of the order of 0.5 M. A study of aluminum chelation was also made under similar conditions. Results indicated only traces of this element were extracted from solutions that were 2.5 M $Al(NO_3)_3$.

A sample of Pu^{VI} that had been oxidized electrolytically was used to determine the percent of this element that would react with TTA under the optimum conditions established for isolating Zr (0.03M TTA, pH 0.2).

[redacted]

Table 5.5-1

Comparison of Zr Chelation with Cb, Ce^{III} and Ru

Aqueous Phase: 0.5M HNO_3, individual tracers
Organic Phase: Equal volume 0.03M TTA Benzene
Equilibration Time: 15 Minutes

Run No.	Tracer Element	Distribution of Activity at Equilibrium (beta c/m/ml) Organic	Aqueous	Distribution Coefficient Org./Aq.
Cb	1-A	40	7.59×10^3	ca. 5.2×10^{-3}
Cb	1-B	30	8.04×10^3	ca. 3.7×10^{-3}
Zr	2-A	1.22×10^3	8.64×10^2	1.4
Zr	2-B	1.0×10^3	9.0×10^2	1.1
Ce^{III}	3-A	5	5×10^5	ca. 10^{-5}
Ce^{III}	3-B	Bkgd.	2.5×10^5	0
Ru	4-A	50	5.1×10^5	ca 10^{-4}
Ru	4-B	1200	1.22×10^6	1.01×10^{-3}

6.0 Flowsheet Separation of Zirconium from Clinton Irradiated Slugs

An irradiated uranium slug was dissolved in HNO_3 acid by the members of the Operations Division and passed through an ion exchange column. Zirconium along with some Cb, Pu and rare earths was eluted with 5% oxalic acid and used as a source of activity to demonstrate the separation process discussed in this report.

Twenty five milliliters of acid solution containing Zr, Cb, Pu, and traces of rare earths were added to a flask fitted with a reflux condenser and made 1.0M in HNO_3. A three-fold excess of the stoichiometric amount of $KMnO_4$ necessary to destroy the oxalic acid was added and the mixture boiled gently for 1 hour. Following this treatment the excess permanganate color was destroyed using 30% hydrogen peroxide and the solution again boiled to remove the slight excess of peroxide (This step would also reduce any extractable form of Ce or Pu). Upon cooling to room temperature the solution was contacted with 0.03M TTA in benzene for 30 minutes. The organic phase was then drawn off and washed for 30 minutes with a solution that was 0.01M in hydroxlamine hydrochloride, 0.5M in HCl, and 0.03M in $FeCl_2$. (This step is the procedure developed by Crandall and Thomas in the chelate process for plutonium for the reduction of Pu^{IV} to Pu^{III} which will then strip from the TTA benzene layer leaving the Zr behind). Finally, the organic extract was diluted to 0.007 M TTA, using benzene, and the zirconium was then stripped with 6.0M HCl with a yield of ca. 80%.

Another run similar to the above was made with the addition of one more step. Following the treatment of the solution with permanganate to destroy oxalates, an excess of aluminum nitrate (ca. 1.0M) was added. This step removed the effect of residual traces of oxalates resulting in a higher (99.0%) yield.

7.0 Recommendations [redacted]

Demonstration of the process discussed in this report has shown that zirconium can be prepared essentially free of plutonium and other activity, and it is recommended that this process be used by the radio-isotopes section in preparing large quantities of this element for shipment.

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