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STUDIES OF QUANTITATIVE METHODS FOR THE SEPARATION AND DETERMINATION OF ZIRCONIUM AND THORIUM IN MAGNESIUM ALLOYS

B. A. RABY, 1/LT USAF

MATERIALS LABORATORY

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FOREWORD

This report was prepared by the Analysis and Measurement Branch. It was initiated under Project No. 7360, "Materials Analysis and Evaluation Techniques," Task No. 73600, "Procedures for Compositional Analysis of Aircraft Alloys." It was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt. B. A. Raby acting as project engineer.

This report covers work conducted from August 1954 to August 1956.

Appreciation is expressed by the author for the suggestions and ideas which many have generously given. Outstanding in this number are Dr. E. K. Hyde of the University of California Radiation Laboratory, Dr. J. S. Fritz of Iowa State College, and Dr. G. John, Mr. C. D. Houston, and Lt. George Latimer of this laboratory.

ABSTRACT

This paper describes the results of a comparative study of analytical methods suitable for the determination of thorium and zirconium in magnesium base alloys.

In addition, this paper describes an attempted amalgamation of selected analytical methods and ion exchange techniques into a scheme for the quantitative analysis of thorium and zirconium in these alloys. Manganese and zinc, common constituents of magnesium base alloys, were carried in the experiments, but only to study their interference in the proposed scheme.

The sample is dissolved in $12\underline{N}$-HCl and the resulting solution is percolated through a column containing Dowex 2-X8 anion exchange resin. Magnesium and thorium pass through the column while zirconium, zinc, and manganese are absorbed. The latter elements are removed by eluting the column with water. The thorium and zirconium in the separated fractions can be determined by means of the complexometric titration methods described by J. S. Fritz.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

H. C. Sullivan

H. C. SULLIVAN
Chief, Analysis & Measurement Branch
Materials Laboratory
Directorate of Research

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INTRODUCTION

With the improvement of aircraft dependent to a large degree upon the available materials of construction, it is inevitable that many new and improved materials, out of which various aircraft components can be fabricated, will be developed. An important class of materials is the one which contains the airframe and skin structural alloys. Improved alloys are being developed from several base metals. One of the best is magnesium and this is being used as the base for a series of new alloys which contain thorium, zirconium, and some rare earths. These alloying constituents improve the grain structure (zirconium) and improve its high temperature strength and creep properties (thorium and the rare earths.)

Quantitative methods for separating and determining manganese and zinc are well developed. However, no attempt was made to study interferences by thorium and zirconium in the determinations of magnesium and zinc. Quantitative methods for separating and determining the rare earths are problems of considerable difficulty and are not considered in this work.

PART A

Comparative Methods for the Quantitative Determination of Zirconium and Thorium

1. Thorium

Although the literature abounds with methods for the quantitative determination of zirconium and thorium (c.f. bibliography 1-60), few studies comparing these various methods have been made. As Beamish and Westland point out (128):

> "A critical study of a large number of gravimetric reagents for thorium would be a desirable contribution. Each year a number of new reagents is reported, but little effort has been made to estimate their relative values."

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In the time available to the author for research on this project, it would have been impossible to try every method available in the literature; so certain criteria were used in selecting those methods which seemed best suited to the situation encountered in this work: (1) the method should be simple and rapid; (2) it should be as inexpensive as possible; (3) it should be capable of determining thorium in the presence of fifty times as much magnesium and amounts of zinc and manganese equal to the thorium.

On the basis of these criteria five reagents for the determination of thorium were selected: oxalic acid, ammonium hydroxide, ferron, benzoic acid, and ethylenediaminetetraacetic acid.

a. Oxalic Acid

Not only is the oxalate precipitation one of the classic methods of determining thorium, it also has the advantage of being a relatively simple technique (12,29,57). Rodden and Warf (57) discuss the interferences associated with this method: (1) The coprecipitation of the rare earths, zirconium, and uranium (IV); (2) The photochemical reduction of the oxalate complexes of UO_2 ; (3) The reduction of gold to the metal; and (4) The occulsion of metals whose oxalates are normally acid soluble, i.e. Ca^{++}, Sr^{++}, Ba^{++}, Mn^{++}, Co^{++}, Ni^{++}, Cu^{++}, Zn^{++}, Ag^{+}, Cd^{++}, Sn^{++}, Pb^{++}, and Si^{+4}. The precipitations were made in the following manner:

> Twenty-five milliliters of a standard thorium solution (details of standardization are in the appendix) were diluted to 200 milliliters and 30 milliliters of $12\underline{N}$ - HCl were added. Four grams of oxalic acid dihydrate and a little filter pulp were added to the boiling solution. After a few minutes of boiling, the solutions were set aside to cool overnight. The solutions were filtered through a # 42 paper. The oxalate precipitates were ignited to ThO_2. The results are tabulated in Table I.

TABLE I

Precipitation of Thorium with Oxalic Acid

mg Th Added	mg Th Found	mg Difference
154.5	151.5	-3.0
154.5	152.9	-1.6
154.5	152.9	-1.6
98.3	97.7	-0.6
98.3	98.3	-0.0
98.3	97.0	-1.3
20.0	19.5	-0.5
20.0	19.4	-0.6
20.0	19.6	-0.4

b. Ammonium Hydroxide

The hydroxide precipitation was selected, because it is potentially the simplest available method. Complexing compounds such as carbonate, tartrate, hydroxy acids, sugars, and glycerols interfere, (56). An excess of ammonium ion prevents the precipitation of the alkalis, alkaline earths, zinc, copper, nickel, and silver; but in many cases multiple precipitations are required to completely separate the interfering elements. By boiling thorium solutions containing sodium azide or sodium thiosulfate, thorium hydroxide is precipitated while interfering ions stay in solution. The addition of hexamethylene tetraamine to a boiling solution of thorium will separate the thorium as the hydroxide from the rare earths, cerium, and partially from uranium, scandium, titanium, or zirconium. The hydroxide precipitations were made in the following manner:

> To twenty-five milliliters of standard thorium solution was added enough 6N ammonium hydroxide to ensure precipitation (approximately pH 5) of the thorium. The hydroxide was filtered through a # 41 paper, washed thoroughly with NH_4OH and ignited to the oxide. The results are found in Table II.

TABLE II

Precipitation of Thorium with Ammonium Hydroxide

mg Th Added	mg Th Found	mg Difference
154.5	152.5	-2.0
154.5	152.3	-2.2
154.5	153.2	-1.3
98.3	98.1	-0.2
98.3	98.2	-0.1
98.3	97.5	-0.8
50.0	50.4	+0.4
50.0	50.2	+0.2
50.0	50.2	+0.2
20.0	20.0	-0.0
20.0	19.7	-0.3
20.0	19.8	-0.2

c. Ferron (8 - **hydroxy** - 7 - iodo - quinoline - 5 - sulfonic acid)

The literature indicates that ferron is a fairly specific and easy to use analytical reagent for thorium. Beamish, Mc Donnell, and Ryan (11) claim that in the pH range suitable for thorium, only silver, mercury, and copper interfere while lanthanum, cerium, titanium, nickel, cobalt, and uranium do not. The precipitations were performed in the following manner:

> Twenty-five milliliters of standard thorium solution were diluted to 100 milliliters. A few drops of bromophenol blue were added; then 10% ammonium acetate was added to the solution until the indicator turned blue, and then enough dilute hydrochloric acid until the indicator just turned yellow. After the solution was heated to 70°C, a 0.2% aqueous ferron solution (4 milliliters per milligram thorium) was added, and the solution digested for half an hour. It was then filtered through a # 42 paper and the precipitate was washed with 0.02% ferron solution. The precipitate was ignited to ThO_2. The results of these precipitations are found in Table III.

TABLE III

Ferron Precipitation of Thorium

mg Th Added	mg Th Found	mg Difference
154.5	150.4	-4.1
154.5	151.7	-2.8
98.3	98.6	+0.3
98.3	94.6	-3.7
98.3	95.9	-2.4
50.0	46.8	-3.2
50.0	39.3	-10.7
50.0	33.9	-16.1
20.0	19.8	-0.2
20.0	19.5	-0.5
20.0	19.2	-0.8

d. Ammonium Benzoate

One of the more recent gravimetric techniques for thorium is precipitation as the benzoate (45,52). Rao, et. al (52) recommend the use of benzoic acid to separate thorium from the rare earths. Loucks, et. al (45) find that zirconium benzoate is quantitatively precipitated with the thorium. The benzoate precipitations were made in the following manner:

> To twenty-five milliliters of standard thorium solution were added 75 milliliters of distilled water and a few drops of bromophenol blue. The acidity was adjusted until the solution was just acid to the indicator; 10 grams of NH_4Cl were added and the solution was heated to boiling. One hundred milliliters of hot 2% ammonium benzoate solution were added, and the resulting solution was heated for 10 minutes. The precipitate was allowed to settle, the solution filtered through a # 41 paper, and the residue was washed with 0.5% ammonium benzoate. The precipitate was ignited to ThO_2. The results are tabulated in Table IV.

TABLE IV

Benzoate Precipitation of Thorium

mg Th Taken	mg Th Found	mg Difference
98.3	98.6	+0.3
98.3	98.6	+0.3
98.3	98.7	+0.4
20.0	20.0	+0.0
20.0	19.8	+0.2
20.0	20.0	+0.0

e. The Complexometric Titration of Thorium

This determination depends upon the competition between the thorium complex of Alizarin Red-S and ethylenedinitrilotetraacetate ion (EDTA or Versene). A solution of thorium and Alizarin Red-S has a pink color between pH2 and pH3. This pink color is not to be confused with the basic color of the dye above pH 3.5. The pink complex is titrated with a standardized EDTA solution and when the EDTA has removed all of the thorium from the Alizarin Red-S complex, the color of the solution changes from pink to yellow. Experience at this laboratory has shown that the color change is sometimes rather subtle. The details of the titration are given in Ford and Fritz's article along with a detailed study of the interferences in this method. They include a list of the pK values for the metals (the logarithm of the equilibrium constant for the reaction: Metal + EDTA $\rightleftarrows$ Metal Chelate (132). The metals which interfere (24-28) are, Pb^{++}, Cu^{++}, Ni^{++}, Fe^{++}, Ti^{+4}, Zr^{+4}, Ce^{+4}, V^{+5}, Sn^{+4}, Bi^{+++}.

Aluminum does not interfere if it is present in concentrations less than .01M and if the pH at the endpoint is near 2.4 - 2.5, but larger amounts of aluminum may have to be separated. Anions which form precipitates or complexes with thorium such as phosphate, fluoride, oxalate, sulfate, and mandelate cannot be tolerated. Small amounts of acetate do not interfere, but larger amounts cause a poor endpoint and low results.

The following ions do not interfere: Na^{+}, Li^{+}, Ba^{++}, Mg^{++}, Ca^{++}, Mn^{++}, La^{++}, Co^{++}, Cd^{++}, Zn^{++}, K^{+}, Sr^{++}, Cr^{+++}, Ag^{+}, UO_2^{++}.

The initial standardization of the EDTA solutions was the most difficult problem. A standard $KMnO_4$ solution (142) was used to standardize a $CaCl_2$ solution (141); the calcium standard was then used to standardize the EDTA (134). The standard thorium solution was used to check the titer of the EDTA. The two different methods gave checks to .0001N. In addition, since EDTA may be standardized against a primary standard of weighed zinc metal (127), the titer was checked in this way and the results also agreed to 0.0001N with the other two determinations.

The determination of thorium with EDTA is done in the following manner:

A standard solution of thorium was placed in a 250 milliliter beaker and diluted to about 100 milliliters. A few drops of 0.2% Alizarin Red-S solution were added and the solution's pH was adjusted to about 2.5. The EDTA was delivered from a ten milliliter buret calibrated to 0.05 ml and readable to 0.01 ml. When the pink color began to fade rapidly, the pH was adjusted to 2.8 and the titration was continued until the color changed from pink to yellow. All pH adjustments were made with dilute $HClO_4$ or NH_4OH. The results are to be found in Table V. A pH meter and magnetic stirring greatly aid the titration.

TABLE V

Complexometric Titration of Thorium

mg Th Added	mg Th Found	mg Difference
98.3	98.3	0.0
98.3	98.4	+0.1
98.3	98.3	0.0

Since more detailed studies of this particular determination were conducted later, only three determinations using this method are included in this section.

f. Comparison of the Five Methods for Determining Thorium

Table VI shows the accuracy and precision that this laboratory has achieved with each method.

TABLE VI

Comparison of Methods for Determining Thorium

Method	% Precision	% Accuracy
Oxalate	0.45	1.63
Hydroxide	0.40	0.80
Ferron	3.57	6.67
Benzoate	0.26	0.40
EDTA	0.03	0.03

g. Study of Magnesium Interference in the Precipitation of Thorium Hydroxide

In the investigation of the possible interference of magnesium in the precipitation of thorium with ammonia, two studies were made. One was the effect of different weight-percents of magnesium on the precipitation of thorium at a constant pH; the second was the effect of different pH on the precipitation of thorium in the presence of a large amount of magnesium.

> A series of double hydroxide precipitations were performed in the following manner: First various synthetic Mg-Th solutions were prepared in which the magnesium ranged from 0 to 98 weight percent. To these solutions (at least 100 milliliters in volume) enough NH_4Cl was added to be equal to five times the weight of magnesium present.
>
> A few drops of indicator were added. Three indicators were used: Congo Red - pH range of 3 to 5; phenolphthalein - pH range of 8 to 10; and bromocresol green mixed with methyl red - a sharp color change at pH of 5.1. The mixed indicator was preferred because of its sharp color change. In addition one series of precipitations were performed without any indicator.

Reagent grade ammonium hydroxide was added until the indicator just turned to its basic color. The gelatinous thorium precipitate was allowed to coagulate and settle; then it was filtered on a hard, coarse, ashless # 41 H paper. The beaker and filter paper were thoroughly washed with a solution containing 10 grams of NH_4Cl per liter and enough NH_4OH to make it basic relative to the corresponding indicator used. The hydroxide precipitate was then dissolved from the paper in a minimum of 6N-HCl.

The hydroxide precipitation was repeated using only about 2/5 as much NH_4Cl. The original filter paper was rinsed with NH_4Cl-NH_4OH wash solution so that an acid condition would not dissolve part of the reprecipitated thorium. The precipitate was then filtered and washed. After the precipitate had dried, it was placed in a weighed crucible, the paper was charred, then it was ignited for an hour at 1000°C. The results are found in Table VII and an illustration of these results is found in Figure 1.

The data presented in Table VII and Figure 1 show that the results of these precipitations were consistently high. It can be seen that the error increases with increasing amounts of magnesium, lies between 0.1% and 0.5% of the total metal present, and approaches a maximum of 5-10% of the thorium.

These findings are contrary to the literature (56) which states that magnesium is held back by sufficient ammonium ion. It may be that it is necessary to precipitate thorium hydroxide slowly by some means like the hot solution hydrolysis of urea. The literature is not clear on this point.

TABLE VII

Interference of Magnesium in the Precipitation of Thorium Hydroxide

Indicator	mg Mg Added	Wt. Percent Thorium	mg Th Added	mg Th Found	% Error of Th
Phenolphthalein	48.7	50.8	50.3	50.3	0.0
Phenolphthalein	48.7	50.8	50.3	50.6	0.6
Phenolphthalein	48.7	50.8	50.3	50.4	0.2
Mixed	97.4	34.2	50.5	51.5	2.0
Mixed	97.4	34.2	50.5	51.1	1.2
Mixed	97.4	34.2	50.5	51.1	1.2
Mixed	122.8	29.2	50.5	51.4	1.8
Mixed	122.8	29.2	50.5	50.7	0.4
Mixed	122.8	29.2	50.5	51.1	1.2
Mixed	237.5	17.5	50.5	51.4	1.8
Mixed	237.5	17.5	50.5	51.2	1.4
Phenolphthalein	243.5	17.1	50.3	51.1	1.6
Phenolphthalein	243.5	17.1	50.3	51.1	1.6
Phenolphthalein	243.5	17.1	50.3	51.4	2.2
Mixed	475.0	9.6	50.5	51.9	2.8
Mixed	475.0	9.6	50.5	51.1	2.0
Phenolphthalein	974.0	4.9	50.3	53.3	6.0
Phenolphthalein	974.0	4.9	50.3	53.5	6.3
Phenolphthalein	974.0	4.9	50.3	54.0	7.3
Phenolphthalein	974.0	4.9	50.3	52.2	3.8
Phenolphthalein	974.0	4.9	50.3	53.7	6.8
Phenolphthalein	974.0	4.9	50.3	53.6	6.6
Congo Red	974.0	4.9	50.3	52.5	4.4
Congo Red	974.0	4.9	50.3	52.2	3.8
Congo Red	974.0	4.9	50.3	52.3	3.8

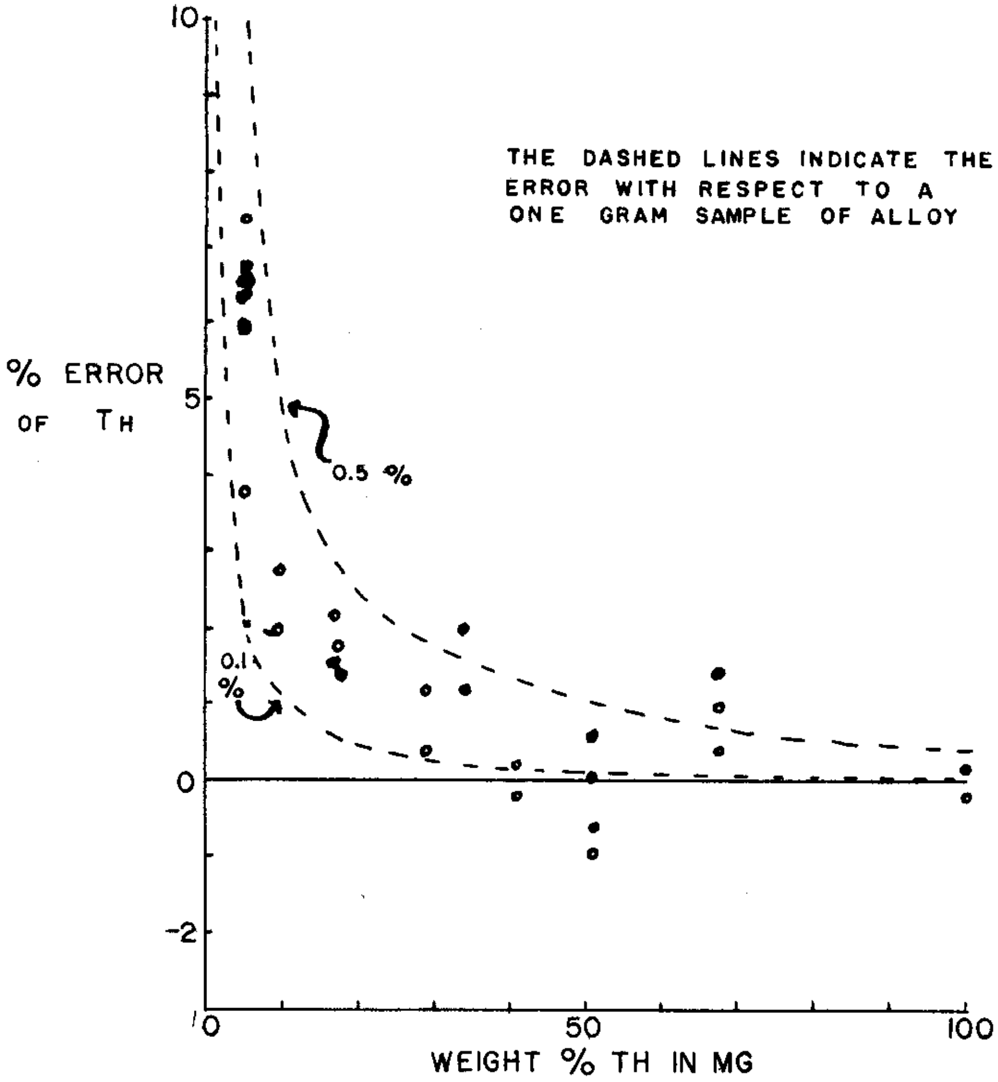

FIGURE I— INTERFERENCE OF MAGNESIUM IN THE PRECIPITATION OF THORIUM HYDROXIDE

From these data no conclusions can be reached about the effect of pH on the carrying of magnesium.

h. The Study of Magnesium, Manganese, and Zinc Interferences in the Complexometric Titration of Thorium

As has already been explained, the complexometric titration of thorium with EDTA depends upon the competition between thorium complexes of Alizarin Red-S and EDTA. One must know whether other ions compete with thorium and, if so, what ions thus interfere.

Solutions containing known compositions of thorium and magnesium (143,144) in dilute acid solution (1N) were titrated with standard EDTA using the method described on page 7 of this paper. Table VIII gives the pertinent data taken from the experiments and shows (Fig. 2) the method is free of interference of magnesium up to 98 weight-percent.

TABLE VIII

Complexometric Titration of Thorium in the Presence of Magnesium

mg Mg Added	mg Th Added	mg Th Found	% Error in Th
47.5	50.5	50.4	-0.2
47.5	50.5	50.6	+0.2
142.5	40.4	40.4	+0.0
142.5	40.4	40.3	-0.2
142.5	40.4	40.5	+0.2
475.0	10.1	10.1	0.0
475.0	10.1	10.3	+2.0
475.0	10.1	10.1	0.0
475.0	20.2	20.2	0.0
475.0	20.2	20.0	- 1.0
None	50.5	50.8	+ 0.6
None	50.5	50.5	0.0
None	50.5	50.5	0.0
None	50.5	50.4	- 0.2

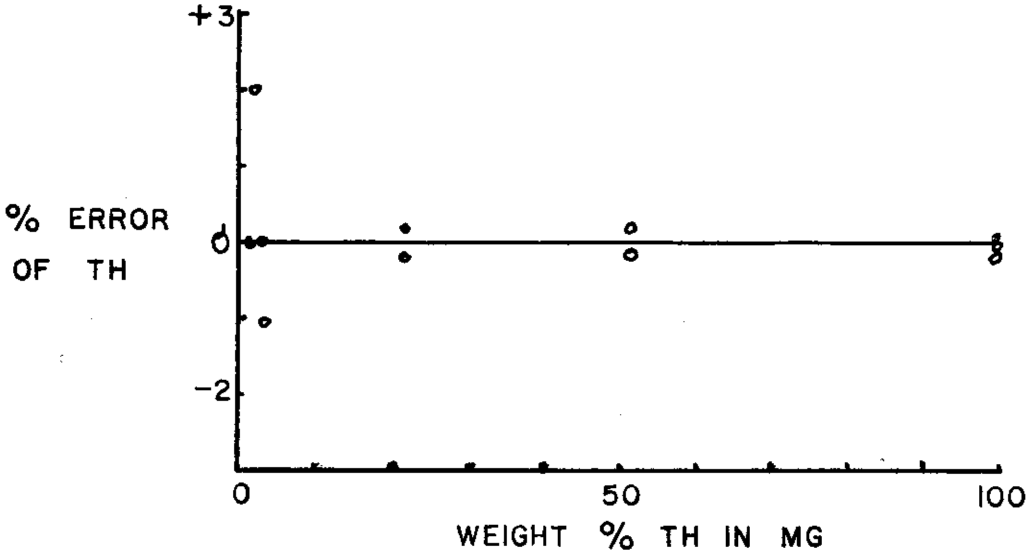

FIGURE 2— COMPLEXOMETRIC TITRATION OF THORIUM IN THE PRESENCE OF MAGNESIUM

Additional experiments were conducted to determine whether manganese and zinc interfere in the titration. The solutions analyzed in the experiments outlined in Table IX were initially 12 N in HCl and contained the maximum expected amount of other elements. Here the first practical difficulty was encountered. Since the titration was to be performed at a pH of 2.8, the acid strength had to be drastically reduced. Two methods were tried. The first was to evaporate the solution to a minimum volume and then dilute the solution to 100 ml volume; the other alternative was to directly neutralize the acid by the addition of ammonium hydroxide. Both methods were tried, but in neither case was an endpoint observed in the titration. Although interference from foreign ions was considered unlikely, the dye, the thorium nitrate, and the EDTA were analyzed spectrographically; no interfering ions were found. No attempt was made to test for possible interfering anions, but they were considered unlikely.

A second explanation of the difficulty was suggested by Dr. Fritz. He thought that since thorium hydrolyzes easily, heat or a momentary excess of base would contribute to the formation of invisible colloidal precipitates of basic thorium salts. Colloidal precipitates mask the complexometric endpoint because the Alizarin Red-S is absorbed on the colloidal particles and this absorption product has the same color as the thorium Alizarin Red-S complex. Since the colloidal thorium does not complex rapidly with the EDTA, the absorbed Alizarin-Red retains its pink color in the presence of four (4) times the required amount EDTA. (It was discovered, however, that an addition of excess EDTA to the colloidal thorium solution containing no Alizarin Red-S present followed by back titration of the excess EDTA with a standard bismuth solution gave the correct results.) In order to prevent formation of colloidal thorium precipitates, Dr. Fritz suggested that the evaporation of the solutions be carried out in the presence of $HClO_4$. When this was tried and no endpoint was detected, it was decided that the buffering action of NH_4ClO_4 formed in adjusting the solution to pH 2.8 dulls the endpoint. Such a phenomenon is known (26).

A satisfactory answer to this problem was obtained by carefully evaporating the solution to about 30 ml <u>without adding $HClO_4$.</u> The resulting solution was diluted with water to about 100 ml and the pH <u>carefully</u> adjusted with NH_4OH. As can be seen from Table IX, this latter procedure gave good results.

TABLE IX

Complexometric Titration of Thorium
in the Presence of Manganese, Magnesium
Zinc, and 12 N - HCl

mg Mg Added	mg Mn Added	mg Zn Added	mg Th Added	mg Th Found
			49.5	49.5
	50		49.5	49.6
		50	49.5	49.5
	50	50	49.5	49.4
1000			49.5	49.5
1000	50	50	49.5	49.7
1000	50	50	49.5	49.6
1000	50	50	49.5	49.6
1000	50	50	49.5	49.5

i. Conclusions and Summary for the Quantitative Analysis of Thorium

This laboratory has found that the easiest and best method for the determination of thorium is the complexometric titration. One must, however, observe the cautions detailed in the preceeding test. The benzoate and hydroxide methods were found to be fairly good and they are relatively easy to perform. The major drawback is the occlusion of magnesium in thorium hydroxide precipitates. Although the thorium oxalate precipitations are reproducible, the results are not accurate. Thorium ferronate is difficult to precipitate and the results are neither reproducible nor accurate.

Even though the EDTA titration for thorium is considered the best method, it will be seen that work described later in this paper does not make use of the method. Those experiments were performed before the titration had been investigated and belong to earlier phases of the work done in this laboratory.

2. Zirconium

The diversity of analytical methods for zirconium (61-103) is nearly as great as for thorium and the need for a comparative study of these methods is also as desirable. Here, as in the case of thorium, time limited the number of methods which could be studied; consequently, the same criteria which governed the selection of the methods for thorium governed the selection of analytical methods for the determination of zirconium. It should be pointed out that no allowance was made for one error which is present in any determination of zirconium: the presence of variable amounts of hafnium found in all but specially purified zirconium preparations. Since the chemistry of hafnium is so similar to that of zirconium, hafnium behaves as zirconium does; therefore, all zirconium standards were assumed to contain pure zirconium.

Following the pattern set in the examination of methods for determining thorium, five analytical methods for determining zirconium were compared. Four gravimetric methods were selected: precipitation of the zirconium with ammonium hydroxide, precipitation of zirconium as the phosphate, and precipitations of zirconium both by benzoic acid and by p-bromomandelic acid. In addition, the titration of zirconium with EDTA was selected to illustrate a volumetric method.

a. Ammonium Hydroxide

The ammonium hydroxide precipitation was chosen because of its simplicity. On the basis of the similarities of the tetravalent states of the elements, one would expect the procedure for the formation of the gelatinous zirconium hydroxide to be the same as for the thorium. The major difference, confirmed at this laboratory, is the formation of the zirconium compound at a lower pH. Since the procedure used for the determination of zirconium was identical to that for thorium, the procedure is not described in detail. The results are given in Table X.

TABLE X

Precipitation of Zirconium with Ammonium Hydroxide

mg Zr Added	mg Zr Found	mg Difference
113.0	113.4	+0.4
113.0	113.4	+0.4
113.0	112.9	-0.1
56.5	56.2	-0.3
56.5	56.2	-0.3
56.5	56.1	-0.4
56.5	56.2	-0.3
56.5	56.3	-0.2
56.5	56.3	-0.2
28.4	28.7	+0.3
28.4	28.7	+0.3
28.4	28.4	0.0
25.8	25.8	0.0
25.8	25.8	0.0
25.8	25.8	0.0

b. Diammonium Hydrogen Phosphate

One of the classical methods for determination of zirconium is precipitation as the phosphate followed by ignition to the pyrophosphate, ZrP_2O_7. The phosphate precipitations were made in the following manner.

> Enough concentrated sulfuric acid (about 11 ml) was added to 100 ml of a hydrochloric acid solution containing a known amount of zirconium (See appendix) to make the solution ten mole percent in sulfuric acid. Twenty milliliters of water containing 1.5 grams of $(NH_4)_2HPO_4$ were added to the solution. The solution was stirred, allowed to stand for at least two hours, (better if chilled overnight) and filtered through a # 42 paper. The precipitate was ignited at 1000°C for an hour and weighed as ZrP_2O_7. The results are given in Table XI.

TABLE XI

Precipitation of Zirconium as the Pyrophosphate

mg Zr Added	mg Zr Found	mg Difference
113.0	119.1	+ 6.1
113.0	118.3	+ 5.3
113.0	116.6	+ 3.6
56.5	56.9	+ 0.4
56.5	56.4	- 0.1
56.5	56.4	- 0.1
28.4	32.7	+ 4.3
28.4	35.1	+ 6.7
28.4	33.2	+ 4.8

There are several sources of error in this determination. Ti, Nb, Ta, and Ce all interfere (82). Another difficulty is due to the possibility of a variable composition of the weighing form (70,99).

c. Ammonium Benzoate

Although the hydroxide has been observed to precipitate at the pH condition of the benzoate precipitation, the result is the same since the precipitate is ignited to ZrO_2. Since this procedure is identical to that used for thorium, it will not be discussed in detail. The results are given in Table XII.

TABLE XII

Precipitation of Zirconium with Ammonium Benzoate

mg Zr Added	mg Zr Found	mg Error
113.0	112.6	-0.4
113.0	112.3	-0.7
113.0	112.7	-0.3
28.4	28.4	-0.0
28.4	28.4	-0.0
28.4	28.4	-0.0

d. p-Bromomandelic Acid

A gravimetric reagent for zirconium which has recently attracted much attention is mandelic acid and its p-chloro and p-bromo-derivatives (61,64,77, 81,86,87,88,90). Much of the work of Klingenberg, et. al. (86,87,88) has been centered in development of analytical schemes for zirconium in steels and magnesium-base alloys. Kumins (90) reports that the determination of zirconium can be made in the presence of Ti, Fe, Al, Cr, V, Th, Ce, Sn, Ba, Cu, Bi, Sb, and Cd. Hahn (81) extends this list to include separations from Co, Mg, Mn, Hg, Ni, U, and Zn. The work of Gavioli and Traldi (77) confirms Hahn and Kumins. The determinations were performed in the following manner:

> To about 75 or 100 ml of zirconium containing solution, 0.1M reagent (50 ml for each .25 gm of alloy sample) was added. The solution was stirred and then digested at 80°C for twenty minutes. The precipitate was filtered on a # 42 paper and washed ten to twelve times with water. The precipitate was then ignited at 1000°C for an hour and weighed as ZrO_2. The results are given in Table XIII.

TABLE XIII

Precipitation of Zirconium as
the p-Bromomandelate

mg Zr Added	mg Zr Found	mg Difference
28.4	29.5	+1.1
28.4	29.2	+0.8
28.4	29.8	+1.4
5.6	5.9	+0.3
5.6	5.8	+0.2
5.6	6.1	+0.5

e. Complexometric Titration of Zirconium with EDTA

Fritz, et al (74,75) at Iowa State College have developed two rapid titrations for zirconium using EDTA; only one of these methods (74) was tried at this laboratory and the reader is referred to the original papers for the details of the other procedure (75).

In the method examined here, excess standard EDTA was added to the zirconium solution along with some thiourea and the excess EDTA was titrated with a standard bismuth solution at a pH of 2.0 until the first excess bismuth gave a yellow complex with thiourea. This endpoint is a sharp, well-defined change if the pH has been accurately adjusted.

> Ten milliliters of 0.05$\underline{M}$-EDTA were added to a solution containing a known amount of zirconium. The pH was adjusted to 2.0 using 6$\underline{N}$-NH_4OH or 6$\underline{N}$-$HClO_4$ and 1.3 grams of thiourea was added. The excess EDTA was titrated with 0.05$\underline{M}$-$Bi(NO_3)_3$ until the first yellow color was obtained. A pH meter to monitor the pH and a magnetic stirrer are valuable accessories to this titration. The results are found in Table XIV.

TABLE XIV

Complexometric Titration of Zirconium with EDTA and Bismuth

mg Zr Added	mg Zr Found	mg Difference
25.8	25.8	0.0
25.8	25.8	0.0
25.8	25.8	0.0

As has been pointed out on page 14 of this report, thorium can be titrated in the same manner as zirconium.

The anions CNS^-, F^-, PO^{---}, SiO_3^{---}, and SO_4^{--} do not interfere if the solution is treated properly (74). Th^{+4}, As^{+3}, Hg^{++}, Mo^{+6}, Ni^{++}, Fe^{+3}, and Sn^{+4}, interfere (74). Interferences from Al^{+3}, Co^{++}, Ti^{+4}, Nb^{+5}, Ta^{+5} can be eliminated by proper treatment of the solution (74). It was found that the following ions will not interfere with the titrations Ag^+, Ba^{++}, Be^{++}, Ca^{++}, Cd^{++}, Ce^{++}, Cu^{++}, Hg^{++}, K^+, Na^+, Li^+, Mg^{++}, Mn^{++}, La^{+++}, Pb^{++}, Sb^{+++}, Sr^{++}, UO_2^{++}, and Zn^{++}.

Some studies were made to determine the effect of various amounts of manganese and zinc on the complexometric titration of zirconium. Tables XV and XVI and Figure 3, give the data from these experiments.

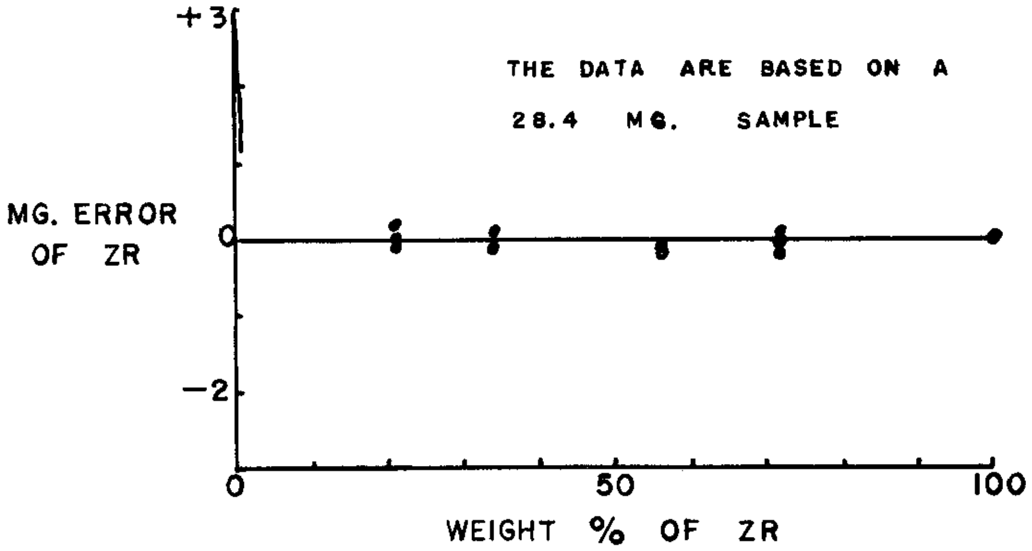

FIGURE 3— COMPLEXOMETRIC TITRATION OF ZIRCONIUM IN THE PRESENCE OF MANGANESE AND ZINC (28.4 MG. ZR)

TABLE XV

Complexometric Titration of Zirconium in the Presence of Zinc

mg Zn Added	% Zr	mg Zr Added	mg Zr Found	mg Difference
10	72	25.8	25.9	+0.1
10	72	25.8	25.7	-0.6
20	56	25.8	25.7	-0.1
20	56	25.8	25.7	-0.1
50	34	25.8	25.8	0.0
50	34	25.8	25.9	+0.1
100	21	25.8	26.0	+0.2
100	21	25.8	25.8	0.0

TABLE XVI

Complexometric Titration of Zirconium in the Presence of Manganese

mg Mn Added	% Zr	mg Zr Added	mg Zr Found	mg Difference
10	72	25.8	25.6	-0.2
10	72	25.8	25.7	-0.1
20	56	25.8	25.6	-0.2
20	56	25.8	25.7	-0.1
50	34	25.8	25.7	-0.1
50	34	25.8	25.7	-0.1
100	21	25.8	25.7	-0.1
100	21	25.8	25.7	-0.1

It should be noted that increasing amounts of zinc tend to slow the color change at the endpoint. Hence, one should be careful that equilibrium has been reached before adding more bismuth. The color fades slowly in the presence of zinc, so that yellow color should persist for at least one minute when the endpoint has been reached.

f. Comparison of Analytical Methods for Zirconium

Table XVII compares the results obtained by these analytical methods.

TABLE XVII

Comparison of Methods for Zirconium

Method	% Precision	% Accuracy
Hydroxide	0.20	0.35
Phosphate	1.32	7.76
Benzoate	0.00	0.00
p-Bromomandelate	0.43	4.62
EDTA Titration	0.00	0.00

g. Study of Magnesium Interferences in the Precipitation of Zirconium Hydroxide

This laboratory was interested in knowing whether magnesium is carried down in the precipitation of zirconium hydroxide. The procedures in these experiments were identical to those in the corresponding thorium experiments; therefore, reference is made to those particular portions of this paper. The assumption was made that zirconium would constitute about one weight percent of a magnesium alloy.

TABLE XVIII

Interference of Magnesium in the Precipitation of Zirconium Hydroxide

mg Mg Added	mg Zr Added	mg Zr Found
5000	56.5	62.5
5000	56.5	63.1
5000	56.5	62.7
4500	56.5	62.5
5000	56.5	63.5
5000	56.5	63.2
1000	11.3	12.3
1000	11.3	12.9
1000	11.3	13.0
1000	11.3	12.0
1000	11.3	13.2
1000	11.3	12.5

It is obvious from these data that a large amount of magnesium is being carried on the zirconium hydroxide. Not only is magnesium included in the zirconium precipitate, but also one would expect zinc and manganese to precipitate. Therefore, this method of determination was abandoned.

h. The Ageing of Zirconium Solutions

During the original standardization of the zirconium solutions it was noted that ignition values (this standardization procedure is described in the appendix) of the solution gave a titer of 1.14 milligrams of zirconium per milliliter of solution while the average of five determinations by EDTA gave a titer of 1.04 milligrams of zirconium per milliliter. The results were checked again using different EDTA and $Bi(NO_3)_3$ solutions; this time the titer value was 1.02 mg Zr/ml. The same solutions were then used to titrate another zirconium solution whose titer was known to be 2.58 mg Zr/ml; the average value was 2.46 mg Zr/ml. So all the EDTA and bismuth solutions were checked against primary $ZnCl_2$ solutions and gravimetrically standardized thorium solutions and against each other. Since everything seemed to be in order, the only possibilities remaining were (1) the complexometric titration was not as accurate as claimed, or (2) the titer of the zirconium solutions was changing.

In order to determine whether the titer of the zirconium solution remained constant a fresh solution of $ZrOCl_2$ in 0.1N-HCl was prepared. Immediately upon completion of the preparation, three 25.00 ml aliquots were withdrawn from the solution and analyzed gravimetrically by ignition. At various times thereafter, three 25.00 ml aliquots were removed and analyzed by complexometric titration. The apparent amount of zirconium present decreased for about twenty-four hours and then became constant. Finally three 25.00 ml aliquots were removed and analyzed by ignition. Table XIX and Figure 4 give the results.

TABLE XIX

Ageing of Zirconium Solutions

Method	Hours After Prepn.	mg Zr Found	% Loss
Ignition	0	28.7	0.0
Titration	0.5	28.2	1.8
Titration	1.5	27.8	3.1
Titration	16.5	26.7	7.0
Titration	23.5	25.2	12.2
Titration	43.5	25.0	12.9
Titration	87.5	25.1	12.5
Ignition	88.0	28.5	0.7

The data indicate that the zirconium probably coagulates into some type of colloidal conglomerates or polymers and reacts only partially or slowly with EDTA to form a complex. The author has discovered that this colloidal condition can be destroyed by varying the procedure slightly:

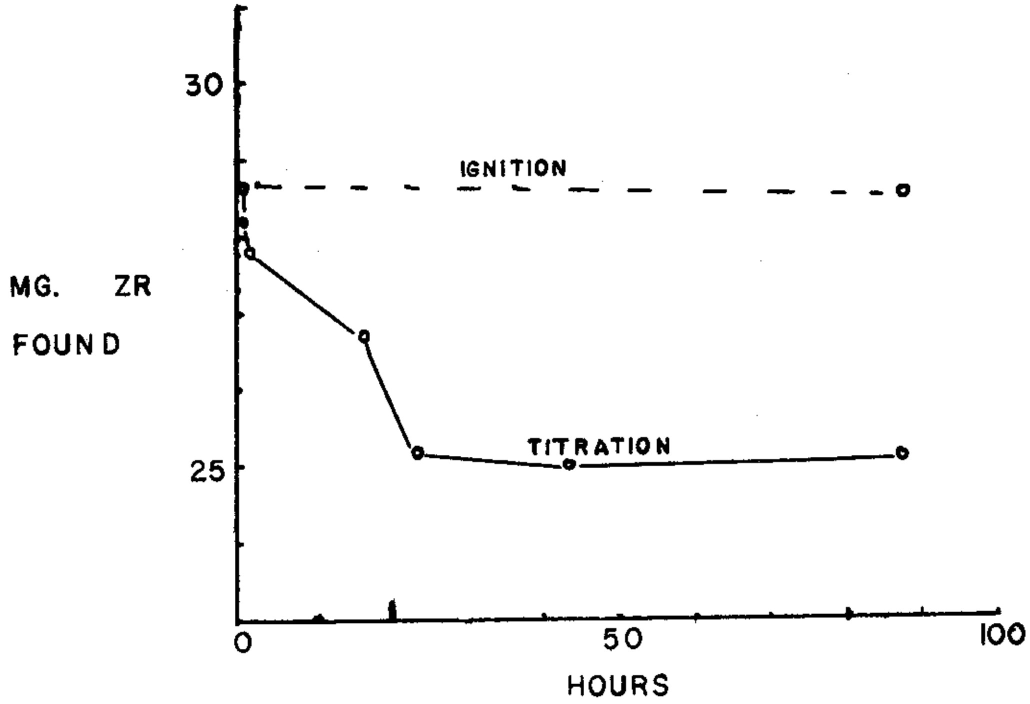

FIGURE 4— AGEING OF ZIRCONIUM SOLUTIONS —

To three 25.00 ml aliquots of the zirconium solution were added twenty milliliters of 0.0524N-EDTA and the volume brought up to 100 ml. Ten drops of 6N-HCl were added and the solution was heated nearly to boiling for 5 to 10 minutes. When the solution had cooled, 1.3 grams of thiourea were added and the bismuth back-titration made. The results gave an average titer of 1.14 mg Zr/ml as compared to a titer of 1.14 mg Zr/ml found by ignition.

Several conclusions about standard zirconium solutions can be drawn from these experiments:

1. The solution should be allowed to stand for several days so that the sorption of zirconium on the glass walls of the container can come to equilibrium.

2. The solution should be standardized both gravimetrically and complexometrically.

3. The reaction of zirconium with the EDTA should be ensured by heating the two together at a pH which prevents precipitation of zirconium hydroxide but which does not destroy the zirconium chelate. A suitable pH is from one to two.

In addition to these notes on the colliodal nature of zirconium solutions, Larsen (91), as a result of his polarographic investigation of zirconium complexes of Alizarin Red-S, has independent evidence of polymer or colloid formation in zirconium solutions.

i. Summary and Conclusions on the Quantitative Analysis of Zirconium

Two methods were found to be quite accurate and precise. They are precipitation of zirconium benzoate and the complexometric titration. Of the two, the titration is the quicker and easier method. One should remember, however, that zirconium hydrolyzes easily and will form colloidal salts. Also to be remembered is the slowness of the titration endpoint in the presence of zinc. The value of the hydroxide precipitation is similar to that of thorium. The precipitations with ammonium phosphate and p-bromomandelic acid have poor accuracy and only fair precision.

In reading the subsequent parts of this paper, it is again to be noted that some of the work was done before the investigation of the EDTA titration. Consequently, one will find various methods being used for the determination of zirconium.

PART B

Ion Exchange Separation of Thorium and Zirconium

The similiarities in the chemistries of zirconium and thorium make their separation and determination tedious and difficult. An examination of the literature (3,59,104,107,109-114,116,120,139,140) indicates that ion exchange techniques could offer, perhaps, the simplest method of separating thorium from zirconium and of separating both of them from other elements, if necessary. Brown and Riemann (105) have separated thorium, titanium, and zirconium from one another by utilizing a pH-buffered citrate elution from a cation exchange resin. Since both zirconium and thorium form polychloro-complex ions, a separation of these elements might be accomplished by use of an anion exchange resin.

If thorium and zirconium could be separated by ion-exchange, they could then be quantitatively determined by the complexometric titrations already discussed.

1. Fundamental Considerations in the Selection and Preparation of Columns Suitable for Ion-exchange

a. Design of a Column

The first factor of importance in ion-exchange techniques is the design of the column. The material must be such that the column can resist corrosion by all chemicals which will be percolated through the resin bed. It must be designed to include all the necessary features required by the experiment, i.e. vapor jackets for heating or special reservoirs or receivers. Last of all, it must be of such size and shape as to hold the necessary amount of resin. Since an optimum geometry in the resin bed is obtained when the length of the bed is about 30 times its diameter (117,119), columns are usually long and thin.

In conformance with these restrictions a number of designs were prepared for this work. In all, some eight basic configurations were built; some of these were constructed in different sizes. The very smallest, used for the preparation of Nb^{95}- free Zr^{95}, was a gravity-flow column measuring 3mm in diameter by 3cm in length and having a small reservoir on top. Several reverse or upward flow columns of both simple and consecutive double units were constructed in order to take advantage of the very gentle agitation which this reverse flow creates in the resin bed. This agitation is supposed to prevent clogging due to particle swelling in strong acid solutions. Unfortunately, it was found that the resin floated in 12N-HCl and that only a coarser resin could alleviate clogging. Another column, similar to a separatory funnel in operation, was constructed to take advantage of batch-type extraction. The low efficiency of the batch process did not allow its use. A large number of columns ranging in capacity from a few milliliters to about two liters were constructed to conform to the ideal dimensions for a column, i.e. the length should be about thirty times the diameter. These particular columns proved to have slow percolation which is theoretically good but not practical and were subject to clogging by swollen resin. Finally, from a consideration of all theoretical and practical aspects of column design the column illustrated in Figure 5, was adopted. It features a fast flow rate which is partially controlled by the screwclamp. It has no stopcocks which might clog up or freeze, and has a glass frit to support the resin bed. The reservoir cap filled with Amberlite IR-4B removes HCl fumes emanating from the reservoir during the sorption and rinse cycles.

b. The Choice of Resins

A survey of the literature (119) reveals that a large number of synthetic ion-exchange resins are available. They are assorted according to particle size, bulk polymeric structure (cross-linkage) and active group; thus it is possible to select a resin almost tailor-made for any situation. Many firms will also discuss the manufacture of special resin products.

Although the theory of ion exchange, including a description of the structure of different resins and their various uses is discussed in detail by Nachod (117) and Samuelson (119), it might be worthwhile to briefly describe these resins for the benefit of those who are not familiar with them. Most resins are three dimensional copolymers. The major portion of the structure is vinylbenzene $(C_6H_5CH\ CH_2)$ while the cross-linkage is roughly proportional to the amount of p-divinylbenzene $(CH_2\ CHC_6H_4CH\ CH_2)$ in the resin. Standard resins usually have cross-linkage (actually percent of p-divinylbenzene) in the amount of 2%,4%,8%, 12%, or 16%. The product is in the form of spherical beads, whose color is dependent upon the active group and the ionic form, and is sieved to standard mesh sizes.

The active group in the resin structure appears on the benzene ring. The cation exchange groups are principally carboxylic acid, phenolic acid, and sulfonic acid; the anion exchange groups are usually some form of a quaternary amine salt. The ionic form of the resin is whatever ion is attached to the active group, but one ionic form is readily converted into another ionic form by percolating a solution of the desired ion through the resin bed.

The porosity of a resin is determined by the amount of cross-linkage in the resin structure. Increasing cross-linkage decreases "hole" size in the resin. The rate with which ions penetrate the resin structure varies with relative sizes of the ions and the "holes" in the polymer. A large ion such as $ZrCl_6^{=}$ or $Cu(NH_3)_4^{++}$ would have more trouble penetrating a resin then would a smaller ion such as Cl^- or Na^+.

The relative affinity of a resin for an ion depends on three factors. The first is the degree of ionization of the resin which is really a measure of the active groups available for exchange. The second depends upon the valency of the exchangeable ions; experiments have shown that the sorption increases with increasing valency. The third depends upon the radius of the ion; again experiments have shown that the sorption increases with increasing atomic weight. Some of the other parameters which also need to be considered are total resin bed capacity, flow rate, and the geometry of the column.

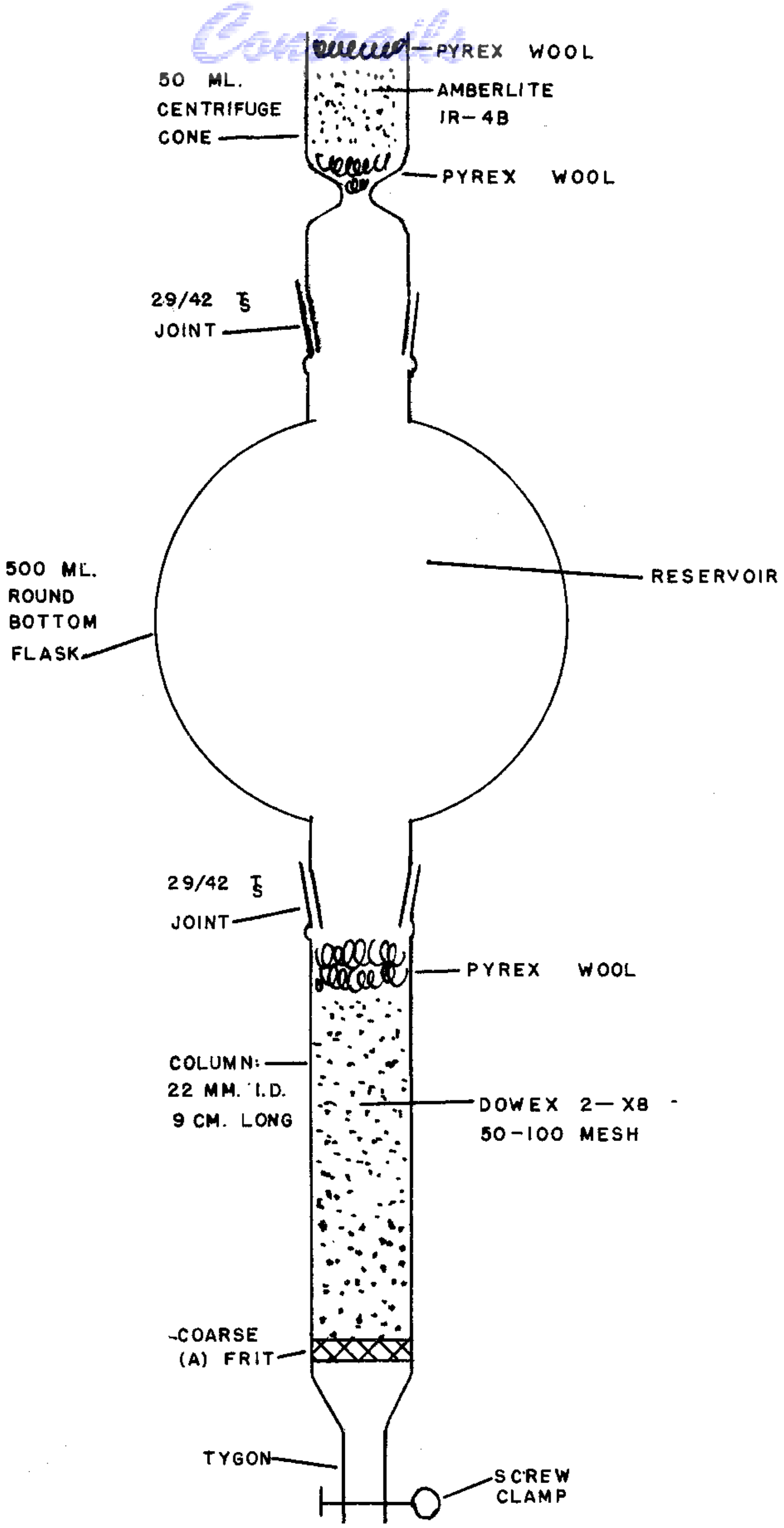

FIGURE 5 --The Ion Exchange Column

A consideration of all these factors led this laboratory to select 50-100 mesh, strongly basic, anion exchange resins (Dowex 1 and Dowex 2). This mesh resin permitted both a good flow rate and good equilibrium and it also had the additional advantage of not clogging the column when swollen with concentrated acid. Resins with porosities (cross-linkages) of four and eight percent were used because of the relatively large sizes of the $ZrCl_6^{=}$, $MnCl_4^{=}$, $ZnCl_4^{=}$, and $ThCl_6^{=}$ ions.

2. Separation of Thorium and Zirconium

The anion exchange separation of polychloro-complexes of zirconium and thorium depends on the fact that the $ZrCl_6^{=}$ ion is strongly sorbed on the column while the weaker $ThCl_6^{=}$ passes on through the column with the effluent (109,110, 113,120,139). After the thorium has been completely eluted, the zirconium can be eluted with weaker solutions of HCl or with water.

In order to establish the actual experimental conditions for separating these elements, a series of experiments involving the sorption and desorption of zirconium and a parallel series involving thorium were conducted.

A known amount of zirconium in 12N-HCl was added to a column (10 mm in diameter and 45 cm long) containing 50-100 mesh resin. This resin was Dowex 1-Z4 and it had been conditioned by pretreatment with 12N-HCl. The column was rinsed with 12N-HCl and desorption performed with 8N-HCl. The data are found in Tables XX and XXI.

In a separate series of experiments, a known amount of thorium in 12N-HCl was added to a column of the same specifications. The column was rinsed with 12N-HCl. The data are in Table XXII.

TABLE XX

Analytical Data for Zirconium Ion Exchange

Experiment Number	mg Zr Found in Sorbtion Effluent	mg Zr Found in Rinse Effluent	mg Zr Found in Desorbtion Effluent	mg Zr Found (total)	mg Zr Added
1	2.0	0.3	56.7	59.0	56.5
2	1.0	0.4	55.7	57.1	56.5
3	0.0	1.8	54.9	56.7	56.5
4	1.1	0.1	56.1	57.3	56.5
5	1.3	0.2	55.7	57.2	56.5
6	1.1	0.0	54.9	56.0	56.5
7	0.0	0.5	12.0	12.5	11.3
8	0.0	0.2	11.9	12.1	11.3
9	0.0	0.1	11.6	11.7	11.3

TABLE XXI

Conditions of Zirconium Experiments

Experiment Number	Sorption [a] Volume (ml)	Rinse [a] Volume (ml)	Desorption [b] Volume (ml)
1	50	25	500
2	50	25	300
3	50	25	500
4	100	200	500
5	100	200	600
6	100	200	600
7	100	400	500
8	100	400	500
9	100	400	500

a. Sorption and rinse solutions were 12 N-HCl

b. Desorption solution was 8 N-HCl

TABLE XXII

Analytical Data for Thorium Ion Exchange

Experiment Number	mg Th [a] Found in Sorption Effluent	mg Th [b] Found in Rinse Effluents	mg Th Found (total)	mg Th [c] Added
1	22.5	8.4	30.9	30.7
2	23.6	7.6	31.2	30.7
3	22.4	8.4	30.9	30.7

a. The sorption effluent was always 100 ml of 12 N-HCl.

b. The rinse effluent was always 500 ml of 12 N-HCl.

c. Two grams of magnesium were added to each solution.

Next a series of experiments was tried in which both elements were present in the same solution.

> In the first set of experiments (A), known amounts of thorium and zirconium plus approximately two grams of magnesium were added to a column (35 cm long and 0.7 cm in diameter) filled with 100-200 mesh resin (Dowex 2-X8). The sorption was made from 100 ml saturated HCl solution and the rinse was made with 25 ml of 12 N-HCl. Desorption of the zirconium was done by percolating 300 ml of H_2O through the bed. Thorium was determined by the hydroxide method and zirconium by the pyrophosphate method.
>
> In the other set of experiments (B), known amounts of thorium and zirconium plus approximately one gram of magnesium were added to a column (45 cm long and 1 cm in diameter) containing 50-100 mesh resin (Dowex 1-X4). Sorption was made from 100 ml of 12 N-HCl solution, the rinse consisted of 400 ml of 12 N-HCl. Desorption was by 300 ml of H_2O. Both thorium and zirconium were determined by the hydroxide method.
>
> Table XXIII contains the analytical data from these experiments:

TABLE XXIII

Analytical Data for Ion Exchange Separation
of Thorium and Zirconium

Experiment	mg ThO_2 Added	mg ThO_2 Found	mg ZrO_2 Added	mg ZrO_2 Found	Total Oxide Added	Total Oxide Found
A - 1	69.4	76.5	15.3	8.0	84.7	84.5
- 2	69.4	72.8	15.3	12.5	84.7	85.3
- 3	69.4	72.1	15.3	8.2	84.7	80.3
B - 1	35.2	38.6	7.6	8.2	42.8	46.8
- 2	35.2	35.5	7.6	8.6	42.8	44.1
- 3	35.2	38.4	7.6	9.7	42.8	48.1

One final experiment on elution of thorium and zirconium in the presence of 50 mg each of manganese and zinc was conducted.

> Sixty ml of 12N-HCl solution containing known amounts of thorium and zirconium plus manganese and zinc was absorbed on the column described in Figure 5. The bed was filled with 50-100 mesh resin (Dowex 2-X8). In the first experiment the rinse consisted of 240 ml of 12N-HCl and the desorption was 200 ml of H_2O. In the second experiment the rinse consisted of 30 ml of 12N-HCl and the desorption was 150 ml of H_2O. The results are found in Table XXIV. Both the thorium and zirconium were determined by complexometric titration.

TABLE XXIV

Analysis of Solutions Containing Thorium,
Zirconium, Zinc and Manganese

Experiment	meq Th Added	meq Th Found	meq Zr Added	meq Zr Found	Total meq Added	Total meq Found
1	.4266	.4306	.6117	.5710	1.0383	1.0016
2	.4266	.3311	.6117	.5401	1.0383	0.8712

3. Relative Elution of Manganese, Zinc, and Zirconium

It is known (139) that manganese and zinc also form strong polychloroanionic complexes; therefore, they should be sorbed on the anion exchange resin with the zirconium.

The experiment described below was performed to obtain an idea of the relative rates of elution as compared to zirconium:

> To 100 ml of 12N-HCl containing $ZrOCl_2$, $ZnCl_2$, and $MnCl_2$ were added tracer amounts of Mn^{54}, Zn^{65}, and Nb^{95}-free Zr^{95}. This solution was put into the reservoir of the column described in Fig. 6. As the solution percolated through the column, it passed a G-M tube detector located at the bottom of the bed. This tube's geometry was limited by a slit in its lead shield so that only activity which passed the slit caused a history of its passage to be recorded on a strip chart connected to the G-M tube. When the effluent left the tip of the column, it was collected in a fraction collector which was set to take six to nine milliliter samples. Each sample was counted for gamma activity and a number were examined with a pulse height analyzer in order to determine the gamma spectra and consequently to identify the isotopes. Comparision of the volumes, the times, the strip chart records, and the data from the fraction collector gave a fairly complete history of the elution of manganese, zinc, and zirconium from the column. A total of ninety-two samples representing an effluent volume of 684 milliliters were analyzed. Figure 7, taken from the fraction collector data, shows the relative elution of the three elements.

4. Summary and Conclusions on Ion Exchange

Not enough variables have been studied in order that a definite statement can be made whether or not an anionic-complex exchange process will quantitatively separate thorium and zirconium in the presence of magnesium, manganese, and zinc. The author feels that such a separation is possible. However, so much time was spent on quantitative methods that ion exchange studies were not completed. The chief difficulty has been that zirconium tends to partially pass through the column with thorium and as a result the thorium fraction is too heavy and the zirconium fraction is too light. It may be that an increased column length and capacity would alleviate the difficulty.

PART C

Summary and Conclusions

This work has had a two fold purpose: first, to investigate and evaluate a number of methods for the quantitative determination of thorium and zirconium and, second, to investigate the feasibility of separating these two elements by anion exchange. In both studies, an attempt was made to evaluate the methods under the conditions which would be present if thorium and zirconium were components of magnesium-base alloys. A comparison of analytical methods

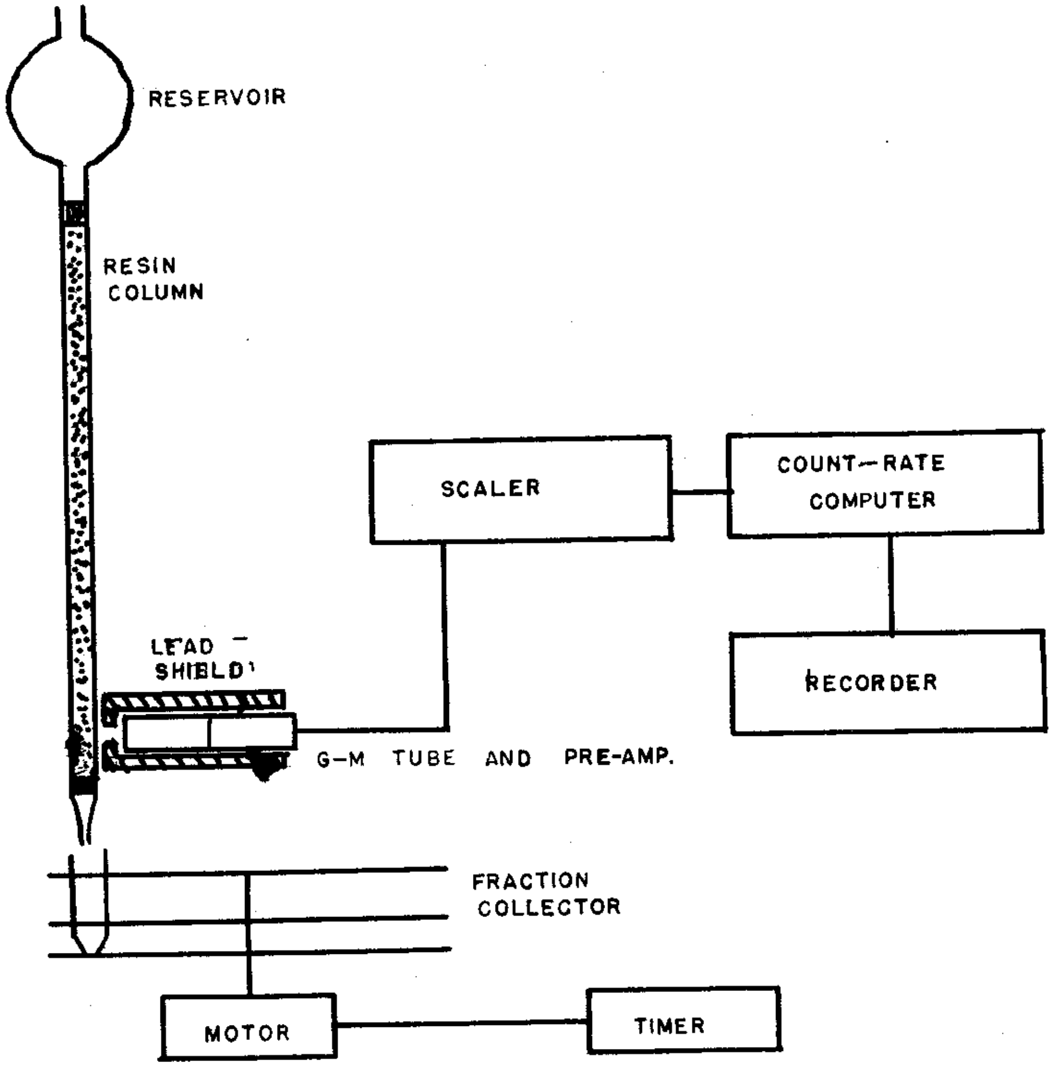

FIGURE 6 -- Schematic Diagram of the Apparatus Used In The Study of the Relative Elution of Mn, Zn, and Zr

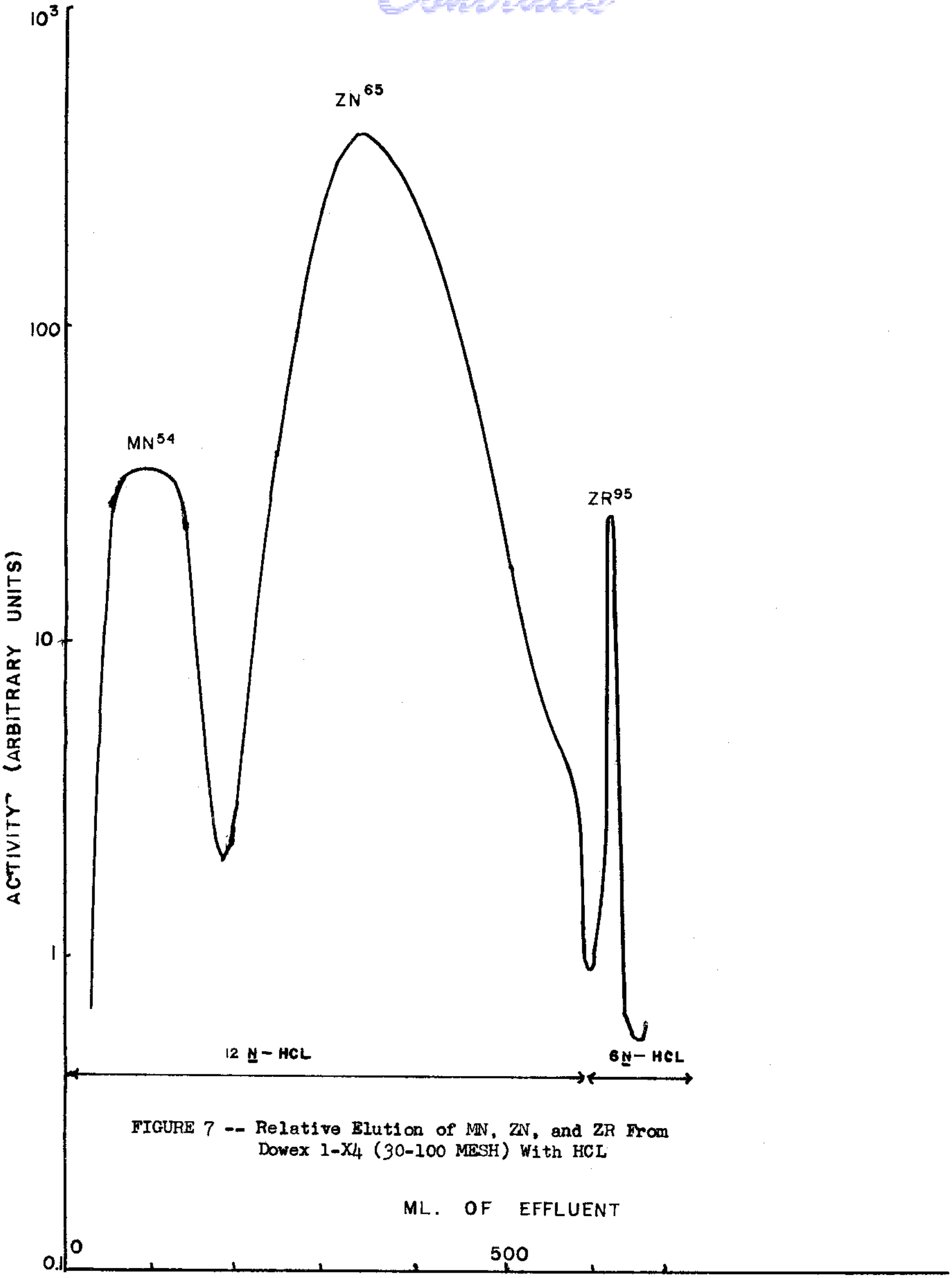

FIGURE 7 -- Relative Elution of MN, ZN, and ZR From Dowex 1-X4 (30-100 MESH) With HCL

for thorium and zirconium demonstrated that the precipitation of both elements as the hydroxides can be subject to considerable error in the presence of magnesium while the complexometric titration of both elements using EDTA showed no such interference. The complexometric titration has the additional advantage of being more rapid and convenient than the gravimetric methods with their attendant digestions, filtrations, ignitions, and weighings. Of the other methods investigated, the ferron precipitation of thorium, the phosphate precipitation of zirconium, and the mandelate precipitation of zirconium are found to be unreliable while precipitation of both elements as the benzoate, and precipitation of thorium as the oxalate, are good, but lengthy.

The ion-exchange separation studies of thorium and zirconium were not wholly successful, but the author feels that not enough of the parameters have been fully investigated. This lack of completeness probably has more than one cause, but essentially the problem proved to be too complex for one person to complete in the time available. It is certainly not thought that the failure of ion-exchange separations has been proven. On the contrary, there is reason to believe that a more complete study of problems involved would lead to the development of a completely satisfactory analytical separation.

APPENDIX

1. Solutions required

a. Thorium

(1) 4.76 gm $Th(NO_3)_4 \cdot 4H_2O$ in 1000 ml 12N-HCl soln. ≅ 2 mg Th/ml.
(2) 4.76 gm $Th(NO_3)_4 \cdot 4H_2O$ in 1000 ml 0.1N-HCl soln. ≅ 2 gm Th/ml.

b. Zirconium

(1) 7.06 gm $ZrOCl_2 \cdot 8H_2O$ in 1000 ml 12N-HCl soln. ≅ 1 mg Zr/ml.
(2) 7.06 gm $ZrOCl_2 \cdot 8H_2O$ in 1000 ml 0.1N-HCl soln. ≅ 1 mg Zr/ml.

c. Magnesium

$$\left.\begin{array}{l} 83.61 \text{ gm } MgOl_2.GH_2O \\ 10.00 \text{ gm Mg} \\ 16.06 \text{ mg MgO} \end{array}\right\} \quad \text{in 1000 ml 12N-HCl soln.} \cong \text{10 mg Mg/ml.}$$

d. Manganese

4.50 gm $MnCl_2 \cdot 4H_2O$ in 125 ml 12N-HCl soln. ≅ 10 mg Mn/ml.

e. Zinc

1.56 gm ZnO in 125 ml 12N-HCl soln. ≅ 10 mg Zn/ml.

f. Versene

9.31 gm disodium versenate dihydrate in 1000 ml. aqueous soln. ≅ 0.05N

g. Bismuth Standard (primary)

5.2250 gm. pure bismuth metal dissolved in enough HNO_3 to prevent hydrolysis when diluted to 1000 ml. This solution is 0.0500 N with respect to bismuth.

h. Zinc Standard (primary)

3.2690 gm pure zinc metal disolved in minimum HCl and diluted to 1000 ml. This solution is 0.0500 N with respect to zinc.

i. Miscellaneous

Other solutions as required in the test will not be listed except those used in the titrations. They are 6N-$HClO_4$ and 6N-NH_4OH. Also one needs a 0.2% aqueous solution of Alizarin Red-S.

2. Standardization of thorium and zirconium solutions by ignition

The procedure for standardization of thorium and zirconium solutions by ignition is given as follows. One pipettes an aliquot portion of the solution which is to be standardized into a weighed crucible. The crucible is placed under a heat lamp and the solution is evaporated carefully to prevent spattering. When the solution has been reduced to dryness, the crucible is ignited at 1000°C for an hour in a furnace. When the crucible has been cooled to room temperature in a desiccator, it is weighed and the amount of thorium or zirconium is calculated from the ThO_2 or ZrO_2 present.

BIBLIOGRAPHY

1. Thorium

1. Airey, Smales, "Method for the Amperometric Titration of Thorium." NSA. Vol. 6. p. 2872; AERE-C/M-131.

2. Athavale, Tillu, "Iodate Determination of Thorium." Anal. Chim. Acta. Vol. 11, (1954). pp. 62-7.

3. Atter, Heumann, Zebroski, "Thorium Complexes with Cl^-, F^-, No_3^-, $PO_4^{\equiv}$, and $SO_4^{=}$." JACS. Vol. 73. (1951). pp. 5646-50.

4. Banerjee, Datta, "Determination of Thorium with Organic Reagents. Different Methods Using p-Aminosalicylic Acid." Anal. Chim. Acta. Vol. 13. (1955). pp. 23-7.

5. Banerjee, Datta, "Estimation of Thorium by Organic Reagents. Part VI. Use of Some Iodobenzoic Acids." J. Indian Chem. Soc. Vol. 32. (1955). pp. 167-172.

6. Banerjee, Datta, "Determination of Thorium by Use of 2,4-Dichlorophenoxyacetic and Guaiacylacetic Acids." J. Indian Chem. Soc. Vol. 31. (1954). pp. 397-401.

7. Banks, Davis, "Analytical Applications of the Reaction of Thorium with Benzenephosphonic Acid." ISC-524. (Sept. 22, 1954).

8. Banks, Diehl, "New Titrimetric Methods for Thorium." Anal. Chem. Vol. 19. (1947). pp. 222.

9. Banks, Edwards, "Analysis of Thorium-Aluminum Alloys." ISC-405. (Sept. 9, 1953).

10. Barney, Fry, Stoughton, "Chemistry of Thorium in Aqueous Solutions. I. The Thorium-Iodate System; Solubility and Complexes." AECD-2429. (Dec. 30, 1948).

11. Beamish, McDonnell, Ryan, "Determination of Thorium and Its Separation from Uranium by Ferron." Anal. Chem. Vol. 19. (1947). p. 416.

12. Bose, Chowdhury, "Physico-chemical Studies on the Complex Formation Between Th(IB) Ion and Oxalate Ion. Part II. Thermoetric and Cryoscopic Titrations." J. Indian Chem. Soc. Vol. 32. (1955). pp. 673-8.

13. Buttler, Isaac, "Use of Th^{234} in the Determination of Thorium." NSA. Vol. 6. 5989; NP-4067.

14. Byerly, Perry, Thomason, "Colorimetric Determination of Microgram Amounts of Thorium Using 1-(O-Arsenophenylazo)-2-naphthol-3,6-disulfonic Acid." Anal. Chem. Vol. 21. (1949). pp. 1239.

15. Cabell, "Complex Ions Formed by Thorium and Uranium with Complexones." NSA. Vol. 6. p. 3771; AERE-C/R-813.

16. Cowan, "Thorium Salicylate Extraction from the Rare Earths." NSA. Vol. 5. p. 3108; AECD-3108; ANL-HDY-564.

17. Crepaz, Marchesini, "Determination of Thorium by m-Nitrobenzoic Acid." Atti. Ist. Veneto. Sci., Classe Sci. Mat. e Nat. Vol. 110. (1952). pp. 33-9.

18. Datta, "Analytical Aspects of Some Organic Compounds. Part I. Some Phenolic Acids in the Estimation of Thorium and Zirconium." J. Indian. Chem. Soc. Vol. 32. (1955). pp. 687-93.

19. Deshmukh, Xavier, "Determination of Thorium by Organic Bases." Bull. Chem. Soc. Japan. Vol. 28. (1955). pp. 233-4.

20. Eberle, Kronstadt, "Analytical Procedure for the Colorimetric Determination of Thorium." NSA. Vol. 6. p. 1401; RMO-838.

21. Eswaranarayana, "Thorium - Its Estimation and Separation from Cerite Earths." Rec. Trav. Chim. Vol. 72. (1953). pp. 1003-6.

22. Eswaranarayana, Rao, "The Oxinates of Thorium and Some Cerite Earths." Anal. Chim. Acta. Vol. 11. (1954). pp. 339-49.

23. Fletcher, Grimaldi, "Thoron - Tartartic Acid Systems for the Spectrographic Determination of Thorium." Anal. Chem. Vol. 28. (1956). pp. 812-816.

24. Ford, Fritz, "A Titrimetric Determination of Thorium." ISC-304. (Jan. 1953).

25. Ford, Fritz, "A Titrimetric Determination of Thorium." ISC-520. (June 1954).

26. Ford, Fritz, "EDTA Complexometric Titration of Thorium." Anal. Chem. Vol. 25. (1953). pp. 1640.

27. Fritz, Ford, "Titrimetric Determination of Thorium." ISC-304. (Jan 1, 1953).

BIBLIOGRAPHY (CONTINUED)

28. Ford (thesis), Fritz, "Titrimetric Determination of Thorium." ISC-520. (June 1954).

29. Gordon, Kall, "Quantitative Insolubility of Thorium Oxalate." Anal. Chem. Vol. 25. (1953). pp. 1256-8.

30. Gordon, Shaver, "Application of Strong Chelating Agents in the Separation of Thorium and the Rare Earths." NYO-3555.

31. Gordon, Stine, "Amperometric Titration for Thorium in the Presence of the Rare Earths of Monazite Sand." NSA. Vol. 6. p. 5316. NYO-3187.

32. Gordon, Stine, "Separation of Thorium Iodate: Precipitation of Iodates from Homogenous Solution." NSA. Vol. 1. p. 4057. NYO-3188.

33. Grimaldi, Levine, "Application of Mesityl Oxide to the Determination of Thorium." NSA. Vol. 5. p. 5116; AECD-3186.

34. Guest, "Determination of Thorium in Residues by Column Method II. Colorimetric Estimation of Small Amounts of Thorium." NSA. Vol. 6. p. 5571; NP-4004, TR-98/52.

35. Hara, West, "High Frequency Titrations Involving Chelation with EDTA. IV. Complexation of Thorium Nitrate." Anal. Chim. Acta. Vol. 13. (1954). pp. 189-94.

36. Hawley, Silverman, "Spectrographic Determination of Zirconium in Thorium." Anal. Chem. Vol. 28. (1956). pp. 806-8.

37. Hseu, Pan, "Potentiometric Titration of Thorium and Cerium Nitrates with a Glass Electrode." Bull. Chem. Soc. Japan. Vol. 28. (1955). pp. 309-12.

38. Johnson, Kolthoff, "Amperometric Titrations of Thorium and Zirconium with m-Nitrophenylarsonic Acid." J. Electrochemical Soc. Vol. 78. (1951). pp. 138-45.

39. Katzin, The Chemistry of Thorium from The Actimide Elements. NNES. IV-14A. pp. 66-102.

40. Krishnamurty, Purushottam, "Vanillic Acid, New Reagent for Thorium." Rec. Trav. Chim. Vol. 71. (1952). pp. 671-5.

41. Krishnamurty, Rao, "Analytical Chemistry of Thorium. Part VII. Separation from Cerite Earths with Anisic Acid." J. Indian Chem. Soc. Vol. 28. (1951) pp. 261-4.

BIBLIOGRAPHY (CONTINUED)

42. Krishnamurty, Venkateswarlu, "Separation of Small Amounts of Thorium from the Cerite Earths of Monazite and Other Elements; Use of Cinnamic Acid." Rec. Trav. Chim. Vol. 71. (1952). pp. 668-70.

43. Lakshminarayana, Rao, "Analytical Chemistry of Thorium. Part IX. Ammonium Furoate and Sodium Sulfanilate." J. Indian Chem. Soc. Vol. 28. (1951). pp. 551-4.

44. Lerner, Petretic, "Separation of Rare Earths from Thorium Nitrate." NSA. Vol. 9. p. 6620; NBL-108.

45. Loucks, Stenger, Walker, Wengert, "Gravimetric Determination of Thorium and Rare Earth Elements in Magnesium Alloys." Anal. Chem. Vol. 24. (1952). p. 1636.

46. Malat, Ryba, Suk, "Volumetric Determination of Thorium with EDTA Using Pyrocatechol Violet Indicator." Chem. Listy. Vol. 48. (1954). pp. 1511-4.

47. Moeller, Ramaniah, "Chemistry of Thorium, V. Observations on 8-Quinolinol Chelates of Thorium." JACS. Vol. 75. (1953). pp. 3946-9.

48. Murty, Rao, "Analytical Chemistry of Thorium. Part VI. Camphoric Acid Separation from Rare Earths." J. Indian Chem. Soc. Vol. 28. (1951). pp. 218-20.

49. Rao, Rao, "Gravimetric Determination of Thorium by Sebacic Acid." Z. Anal. Chem. Vol. 142. (1956). pp. 27-30.

50. Rao, Rao, "Colorimetric Estimation of Thorium with Nitroso-R Salt." J. Sci. Ind. Research. Vol. 14 B. (1955). pp. 278-81.

51. Rao, Rao, "Analytical Chemistry of Thorium. Part III. Separation from Cerite Earths with O-Toluic and Acetylsalicylic Acids." J. Indian Chem. Soc. Vol. 27. (1950). pp. 569-72.

52. Rao, Rao, Venkataramaniah, "Determination of Thorium and Its Separation from the Rare Earths by Benzoic Acid." Analyst. Vol. 77. (1952). pp. 103-5.

53. Rao, Sarma, Alizarin-S, "Reagent for Thorium. Gravimetric, Colorimetric, and Spectrophotometric Study." Anal. Chem. Acta. Vol. 13. (1955). pp. 142-9.

54. Rao, Suryanarayana, "Analytical Chemistry of Thorium. Part VIII. Aliphatic Dicarboxylic Acids." J. Indian Chem. Soc. Vol. 28. (1951). pp. 511-4.

55. Rodden, and Warf, Analysis and Chemistry of Thorium from Analytical Chemistry of the Manhattan Project. NNES. VIII-1, pp. 160-207.

56. Thorium Hydroxide, Ibid. p. 165.

57. Thorium Oxalate, Ibid. pp. 169-71, pp. 183-4.

58. Thorium Ferronate, Ibid. pp. 179-80, pp. 183-4.

59. Stoughton, Waggener, "Chemistry of Thorium in Aqueous Solutions. II. Chloride Complexing as a Function of Ionic Strength." NSA. Vol. 6. p. 1625; AECD-3305; ORNL-1001.

60. "The Determination of Thorium in Mixtures with Iron, Zirconium and Titanium Using 2,4-Dichlorophenoxyacitic Acid." NSA. Vol. 9. p. 2641.

2. Zirconium

61. Astanina, Ostroumov, "Determination of Zirconium with Mandelic Acid." Zhur. Anal. Khim. Vol. 6. #1. (1951). pp. 27-33.

62. Baltz, Kiefer, "Spectrographic Determination of Zirconium." Anal. Chem. Vol. 24. 1952.

63. Barnard, Telford, Analytical Chemistry of Zirconium from Analytical Chemistry of the Manhattan Project. NNES. VIII-1. pp. 474-82.

64. Belcher, Sykes, Tatlow, "Mandelic and Halomandelic Acids as Reagents for the Determination of Zirconium." Anal. Chim. Acta. Vol. 10. (1954). pp. 34-47.

65. Bradshaw, Mayer, "Absorbtiometric Determination of Zirconium by Means of Alizarin-S with Special Reference to Magnesium Alloys." Analyst. Vol. 77. (1952). pp. 476-83.

66. Calichman, Lidewig, "Polarography of Zirconium Salts in Methanol." Anal. Chem. Vol. 25. (1953). pp. 1909-10.

BIBLIOGRAPHY (CONTINUED)

67. "Analytical Aspects of Some Organic Compounds. Part I. Some Phenolic Acids in the Estimation of Thorium and Zirconium." *J. Indian Chem. Soc.* Vol. 32. (1955). pp. 687-93.

68. Dhar, Das Gupta, "Colorimetric and Volumetric Estimation of Zirconium." *J. Sci. Ind. Research.* Vol. 11 B. (1952). pp. 500-1.

69. Dhar, Das Gupta, "Gravimetric Determination of Zirconium with Oxalohydroxamic Acid." *J. Sci. Ind. Research.* Vol. 11 B. (1952). pp. 500-1.

70. Diehl, Willard, *Advanced Quantitative Analysis.*

71. Dunham, Fred, "Determination of Tantalum, Zirconium, and Hafnium in Niobium by the Porous Graphite Method." *NSA.* Vol. 5. p. 3055; *AECD*-3102; *ANL*-HDY-582.

72. Elving, Olson, "Titrimetric Determination of Zirconium in Magnesium Alloys". *Anal. Chem.* Vol. 28. (1956). pp. 251-2.

73. Elving, Olson, "Gravimetric and Titrimetric Determination of Titanium, Zirconium, and Hafnium with Cupferron." *Anal. Chem.* Vol. 27. (1955). p. 1817.

74. Fritz, Johnson, "Volumetric Titration of Zirconium." *Anal. Chem.* Vol. 27, (1955). p. 1653.

75. Fritz, Fulda, "Titrimetric Determination of Zirconium." *ISC*-382. *Anal. Chem.* Vol. 26. (1954). p. 1206.

76. Frost-Jones, Yardley, "Color Reactions Chloranilic Acid with Particular Refer to the Estimation of Calcium and Zirconium." *Analyst.* Vol. 77. (1952). pp. 468-72.

77. Gavioli, Traldi, *J. Iron Steel Inst.* Vol. 167. (1951). p. 167.

78. Graham, Upton, Van Dalen, "Note on the Polarographic Determination of Zirconium." *Can. J. Chem.* Vol. 30. (1952). pp. 1069-72.

79. Grimaldi, White, "Quercetin as a Colorimetric Reagent for the Determination of Zirconium." *Anal. Chem.* Vol. 25. (1953). pp. 1886-90.

80. Gubeli, Jacob, "Colorimetric Determination of Zirconium with Alizarin-S." *Helv. Chim. Acta.* Vol. 38. (1955). pp. 1026-32.

81. Hahn, *Anal. Chem.* Vol. 21. (1949). p. 1579.

BIBLIOGRAPHY (CONTINUED)

82. Hillebrand, Lundell, <u>Applied Inorganic Analysis.</u>

83. Horton, "Spectrophotometric Determination of Zirconium." <u>NSA.</u> Vol. 1. p. 1063; <u>AECD</u>-3482; CF 52-12-62.

84. Hyde, O'Kelley, "Radiochemical and Spectrometer Studies of Several Neutron Deficient Zirconium Isotopes and Their Decay Products." <u>UCRL</u>-1064. (Dec. 28, 1950).

85. Johnson, Kolthoff, "Amperometric Titrations with m-Nitrophenylarsonic Acid." <u>J. Electrochem. Soc.</u> Vol. 98. (1951). pp. 138-45.

86. Klingenberg, Mandel, Vlannes, "Gravimetric Determination of Zirconium Using Mandelic and Benzilic Acids." <u>Anal. Chem.</u> Vol. 26. (1954). pp. 754-6.

87. Klingenberg, Paucci, "Determination of Zirconium in Steels Using p-Bromo- or p-Chloromandelic Acid." <u>Anal. Chem.</u> Vol. 24. (1952). pp. 1861-2.

88. Klingenberg, Papucci, "Determination of Zirconium in Magnesium Alloys Using p-Bromo- or p-Chloromandelic Acid." <u>Anal. Chem.</u> Vol. 27. (1955). pp. 835-6.

89. Kolthoff, Sandell, "Determination of Zirconium as ZrP_2O_7." <u>Textbook of Quant. Inorg. Chem.</u> 2nd Ed. p. 758.

90. Kumins, "Determination of Zirconium in Presence of Interfering Ions." <u>Anal. Chem.</u> Vol. 19. (1947). p. 376.

91. Larsen, "Final Report on The Chemistry of Zirconium and Hafnium." (University of Wisconsin).

92. Nachtrieb, Tobin, "Spectrochemical Analysis of Niobium and Zirconium." <u>NSA</u>. Vol. 5. p. 3056; <u>AECD</u>-3103; <u>ANL</u>-HDY-579.

93. Ostroumov, "New Methods of Chemical Analysis with the Aid of Pyridine, α-Picoline, and Hexamethylenetetraamine." <u>Zavodskaya Lab.</u> Vol. 13. (1947) pp. 404-10; <u>AEC</u>-tr-1755.

94. Rao, Sastry, "Analytical Chemistry of Zirconium. Part III. Salicylic and Phenoxyacetic Acids." <u>J. Indian Chem. Soc.</u> Vol. 28. (1951). pp. 530-2

95. Rao, Venkataramaniah, "Analytical Chemistry of Zirconium. Part I. Benzilic Acid." Ibid. Vol. 28. (1951). pp. 257-60.

96. Rao, Venkateswarlu, "Analytical Chemistry of Zirconium. Part II. Cinnamic Acid." Ibid. Vol. 28. (1951). pp. 354-6.

97. Read, Metallurgy of Zirconium. NNES, VII-4. pp. 687-708.

98. Rhodes, Wilson, "Amperometric Determination of Zirconium with 1-Nitroso-2-napthol." Anal. Chem. Vol. 28. (1956). p. 1199.

99. Safranalsi, Stehney, "Determination of Zirconium with p-Dimethylaminophenylazoarsonic Acid." NSA. Vol. 5. pp. 3050; AECD-3097.

100. Scotts Standard Methods of Chemical Analyses.

101. Templeton, "Colorimetric Determination of Zirconium with Alizarin." NSA. Vol. 5. p. 3047; AECD-3091; ANL-HDY-548.

102. Wengert, "Photometric Determination of Zirconium in Magnesium Alloys." Anal. Chem. Vol. 24. pp. 1449-51 (1952).

103. "Review of the Analytical Chemistry of Zirconium." NSA. Vol. 9. p. 4200.

3. Ion Exchange

104. Benedict, Schumb, Coryell, "Separation of Zirconium and Hafnium." JACS. Vol. 76. (1954). pp. 2036-40.

105. Brown, Riemann, "Separation of Thorium, Titanium, and Zirconium by Ion Exchange." JACS. Vol. 74. (1952). pp. 1278-82.

106. Caddell, Moison, "Performance of Ion Exchange Resins of High Flow Rates." DP-4 (March 1952).

107. Fassell, Hettel, "Determination of Rare Earths in Zirconium. Separation by Ion Exchange." ISC-559; Anal. Chem. Vol. 27 (1955). p.1311.

108. Harris, Khym, Tompkins, "A Study of the Effects of a Number of Column Variables." AECD-2128 (July 19, 1948).

BIBLIOGRAPHY (CONTINUED)

109. Huffman, Iddings, Lilly, "Anion Exchange of Complex Ions of Zirconium, Hafnium, Niobium, and Tantalum." UCRL-1165 (March 2, 1951).

110. Huffman, Lilly, "Anion Exchange Separation of Zirconium and Hafnium." AECD-2714.

111. Iinuma, Iwanaga, "Determination of Thorium in Rare Earths." Research Repts. Fac. Eng. Gifu Univ. #3. (1953). p. 625.

112. Jenkins, "Determination of Thorium in Rare Earths." Analyst. Vol. 80. (1955). pp. 301-13.

113. Kraus, Moore, "Anion Exchange Studies. Separation of Zirconium and Niobium in HCl - HF Mixtures." ORNL-661 (May 25, 1950).

114. Kraus, Phillips, "Anion Exchange Studies. XIX. Anion Exchange Properties of Hydrous ZrO ." JACS. Vol. 78. (1956). p. 249.

115. Lafferty, "Use of Ion Exchange in Analytical Chemistry." AECD-2414 (Nov. 19, 1948).

116. Larsen, Wang, "Separations of Zirconium and Hafnium." JACS. Vol. 76. (1954). pp. 6223-9.

117. Nachod, Ion Exchange: Theory and Application. Academic Press, 1949.

118. Radhakrishna, "Separation of Leanthauum and Thorium by Ion Exchange." Anal. Chim. Acta. Vol. 6 (1952). pp. 351-4.

119. Samuelson, Ion Exchangers in Analytical Chemistry. Wiley & Sons, 1953.

120. Seaborg, Street, "Ion Exchange Separation of Zirconium and Hafnium." AECD-2435.

121. Ion Exchange of Zirconium. NSA. Vol. 5. p. 376.

122. Ion Exchange of Zirconium. Ibid. 1926.

123. Ion Exchange of Zirconium. Ibid. 6702.

124. Ion Exchange of Zirconium. NSA. Vol. 6. p. 83.

125. "Distribution of Zirconium between Cation Exchange Resins and Acid Solutions." NSA. Vol. 8. p. 4021.

126. "Ion Exchange of Zirconium in $HClO_4$ with Amberlite IR-120." NSA. Vol. 8. p. 5816.

4. General

127. Adams, Swann, "Volumetric Determination of Zinc with EDTA." Anal. Chem. Vol. 27. (1955). p. 2005.

128. Beamish, Westland, Anal. Chem. Vol. 28. April Suppl. p. 697.

129. Beamish, Westland, Ibid. p. 700.

130. Bezier, Charlot, Gaughin, Oesper, Rapid Detection of Cations. Chemical Publishing. 1954.

131. Bonner, Wahl, Radioactivity Applied to Chemistry. pp. 145. 151. 298.

132. Calvin, Martell, Chemistry of the Metal Chelates. 1951.

133. Coryell, Sugarman, Radiochemical Studies. The Fission Products. NNES IV-9. pp. 157. 1491-1522. 1752-1760.

134. Diehl, Goetz, Loomis, "Standardization of EDTA". Anal. Chem. Vol. 22. (1950). p. 798.

135. Fiegl, Spot Tests. 2nd Ed. Elsevier Nordemann. p. 1939.

136. Fritz, "Titration of Bismuth with EDTA." Anal. Chem. Vol. 26. (1954). p. 1978.

137. Garrison, Hamilton, "Production and Isolation of Carrier-Free Radioisotopes." UCRL-1067.

138. Hall, Treadwell, Analytical Chemistry. Vol. 1. 9th Eng. Ed. Wiley & Sons. 1948.

139. Hyde, "Some Notes on Radiochemical Separation Methods." pp. 2-3. 14-16, 18-19. Collection of published and unpublished data assembled at UCRL. (June 9, 1953).

140. Hyde, Separation Methods for Thorium from The Actinide Elements. NNES. IV-14A. pp. 544. 552-8.

BIBLIOGRAPHY (CONTINUED)

141. Kolthoff, Sandell, "Standardization of Calcium Solutions." Textbook of Quant. Inorg. Anal. 2nd Ed. pp. 358 and 606.

142. Kolthoff, Sandell, "Standaridzation of $KMnO_4$." Ibid. p. 594.

143. Kolthoff, Sandell, "Determination of Magnesium as $Mg_2P_2O_7$." Ibid. pp. 371-2.

144. Kolthoff, Sandell, "Determination of Magnesium with 8-Quinolinol." Ibid. p. 374.

145. Kolthoff, Sandell, "Mixed pH Indicators." Ibid. p. 451.

146. Los Alamos Chemistry Group. "Collected Radiochemical Procedures." LA-1721.

147. Meinke, "Chemical Procedures Used in Bombardment Work at Berkeley." UCRL-432; AECD-2738; UCRL-2750.

148. Schwartzenbach, "Die Komplexometrische Titration." Die Chemische Analyze, Bd. 45 (1955).