POLAROGRAPHIC METHODS FOR THORIUM AND THEIR APPLICATION TO MAGNESIUM-BASE ALLOYS

POLAROGRAPHIC METHODS FOR THORIUM AND THEIR APPLICATION TO MAGNESIUM-BASE ALLOYS

by

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SCOPE AND CONTENTS:

The precipitation of thorium with certain organic reagents has been shown to afford a basis for polarographic methods for the determination of thorium. Appropriate conditions for the precipitation of thorium by certain reagents have been determined, and the advantages of a homogeneous precipitation of thorium 8-quinolinate have been demonstrated. The precipitate that thorium forms with m-nitrobenzoic acid has been found to be the tetra-m-nitrobenzoate.

The new polarographic methods for thorium have been proven to be directly applicable to zirconium-free magnesium-base alloys. When zirconium is present, a simple anion exchange procedure will eliminate the interference of zirconium, and allow its subsequent determination. The satisfactory nature of the precision and accuracy of the proposed methods, and their applicability to substances other than magnesium-base alloys, have been demonstrated.

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INTRODUCTION

The purpose of this work was to develop new analytical methods, polarographic in nature, for the determination of thorium, particularly in modern magnesium-base aircraft alloys. Some attention was also given to the development of a polarographic method for the determination of zirconium.

(i) Metallurgical Interest in Magnesium-Base Alloys

The effect of zirconium in magnesium-base alloys has been given considerable study by metallurgists in the last fifteen years, and the effect of thorium has been investigated particularly in the last five years. These studies are related to the growth in importance of jet engines during recent years, because there has been a demand from the jet engine industry for "light" alloys with improved performance characteristics, especially at elevated temperatures. The development of new alloys containing thorium and zirconium has, in turn, given rise to a need for improved analytical methods for thorium and zirconium, elements that heretofore have held only modest metallurgical interest.

Zirconium is useful as an alloying constituent in magnesium-base alloys primarily because of its grain-refining ability, which makes possible the casting of alloys that otherwise would be very difficult to handle in the foundry. This grain-refining action also improves the ductility and toughness of the alloys, both at ordinary and elevated temperatures.

Leontis (1) reports that the addition of thorium to magnesium-zirconium alloys results in superior load-carrying ability and the highest creep resistance shown by any magnesium-base alloy. Magnesium-thorium-zirconium alloys possess definite advantages over magnesium-zirconium alloys at 200° to 300°C., and they possess some usefulness at 375°C., a temperature at which magnesium-zirconium alloys would generally not be considered applicable. Recent publications (2,3) indicate that a still further improvement in creep resistance and a further extension of the useful temperature range can be achieved by the addition of zinc to magnesium-thorium-zirconium alloys.

Leontis (4) has shown that alloys containing thorium at about the 3 percent level, together with zirconium at about 0.7 percent, are suitable for many stressed applications at elevated temperatures. In a recent paper, Ball (5) presented data for a magnesium-base alloy, containing 3 percent thorium, 0.7 percent zirconium and 2.5 percent zinc, that showed improved creep resistance.

(ii) Methods for the Determination of Thorium

Interest in the analytical chemistry of thorium has been extremely sporadic. During the latter part of the nineteenth century and early part of the twentieth, thorium compounds were used extensively in the incandescent mantle lamp industry, the average mantle consisting of about 99 percent thorium dioxide. It was during this time that the development of analytical methods for thorium first came into prominence. Decline in the use of such mantles was paralleled by a general decline in interest in the chemistry of thorium.

The recent incorporation of thorium in breeder reactors for the production of ${}_{92}U^{233}$ and the use of thorium as an alloying agent has again focussed attention on the analytical properties of this element.

Several colorimetric methods for the detection of thorium have been proposed but these procedures are not specific. Kaserer (6) reported that as little as 0.1 mg. of thorium in 100 ml. of solution yielded a recognizable yellow colour with 2, 3, 4-trihydroxybenzaldehyde but that zirconium behaved similarly. Aurintricarboxylic acid was found by Middleton (7) to yield a bright red lake with thorium, but this reaction is sensitive to only one part in 10,000 and the method is complicated by the similar behaviour of the rare earth elements and zirconium. Sodium alizarinsulphonate has been reported by Germuth and Mitchell (8) to yield a red colour with thorium ions, but the reaction is sensitive to only one part in 200 and is far from specific. Mayer and Bradshaw (9) have applied the colorimetric procedure of Banks _et_. _al_. (10) using 1-(o-arsonophenylazo)-2-naphthol-3:6-disulphonic acid to the determination of thorium in magnesium-base alloys. This method is claimed to be accurate to within 2 percent; a preliminary separation of thorium and zirconium is necessary.

A trend toward the use of organic precipitants for the gravimetric determination of thorium has developed in the last few years, led notably by a group of Indian chemists. These Indian workers have added a large number of new organic precipitants for thorium to an already too long list. Adipic acid (11), ammonium picrate (12), ammonium furoate, sodium sulphonate (13), o- and p-aminobenzoic acid (14), o-chlorobenzoic acid (15), trimethylgallic acid, phenoxyacetic acid, veratic acid (16), anisic acid (17), 7-hydroxycoumarinyl-4-acetic acid (18), camphoric acid (19), o-toluic acid, acetylsalicylic acid (20), cinammic acid (21), vanillic acid (22), m-cresoxyacetic acid (23), and many others have been reported. None of these reagents appear to be an improvement over the more familiar organic precipitants; they are all subject to interfering ions, especially those of zirconium and the rare earth elements. The use of the more familiar organic acids, fumaric, sebacic, phenylarsonic and m-nitrobenzoic, for the gravimetric determination of thorium has been described by Moeller (24) as time consuming and not of general interest. Moeller further states that 8-quinolinol, although generally suitable for the determination of thorium, is in need of further investigation. Recently Eswaranarayana and Raghava Rao (25) reported that a separation of thorium from cerium and lanthanum could be effected at a pH of 3.9 with 8-quinolinol.

Comparatively few titrimetric methods for the determination of thorium have been reported. All are either involved, highly indirect, or inaccurate. As a consequence, the more accurate although more tedious gravimetric methods are preferred. The precipitation-titrimetric method of Metzger and Zons (26), involving titration of the oxalate with ammonium molybdate, is rapid but is not very accurate. The oxidimetric-oxalate method of Gooch and Kobayashi (27) is accurate, but requires the slow addition of the thorium solution to the oxalic acid solution. The possibility of titration of the thorium 8-quinolinate precipitate with potassium bromide-potassium bromate solution after dissolution in hydrochloric acid has been investigated (28, 29). The bromate titration is apparently accurate, but the difficulties in the use of 8-quinolinol as a precipitant are inherent in this method.

The determination of thorium by methods dependent on radio-activity measurements must of necessity assume that radioactive equilibrium has been established between thorium and its decay products. Such methods, moreover, are complicated by the presence of radioactive substances from other disintegration series, and even reasonably accurate results are difficult to obtain.

Much work has been done with the so-called emanation method (30, 31, 32). This method depends on sweeping the gaseous decay product, thoron ($_{86}Rn^{220}$), out of the solutions to be analyzed and determining its activity by passing the mixed gases through an ionization chamber. Cartledge (30) checked this method against the pyrophosphate procedure (33) and reported a maximum error of 1.5 percent. The disadvantages of this procedure are the costly equipment required and the necessity for radioactive equilibrium. Daton et. al. (34) have recently reported refined studies on the radiometric determination of thorium and found scintillation counting of $_{82}Pb^{212}$ and $_{83}Bi^{212}$ (ThB and ThC) to have a much greater sensitivity than thoron-gas counting. A standard error of ±15 percent is reported.

One polarographic method for the determination of thorium has been reported, by Komarek (35). In this method, thorium is precipitated as the iodate, the precipitate is dissolved in sodium hydroxide, and the iodate determined polarographically. The high solubility of thorium iodate in the absence of a large excess of iodate ions leaves this procedure open to criticism.

Tilton and Aldrich (36) describe a mass spectrometric determination of thorium, using the isotope dilution technique, that permits the accurate determination of microgram and submicrogram quantities of thorium.

The time required for each determination is three to five days.

The development of clean-cut analytical methods for thorium has been slow, and present day procedures are not very satisfactory. There is a need for a rapid, precise, and accurate method for thorium, with particular reference to its determination in magnesium-base alloys.

(iii) Methods for the Determination of Zirconium

The recent use of zirconium in nuclear reactors and its incorporation in certain alloys has directed attention to the analytical chemistry of this element. The analytical chemistry of zirconium is similar to that of thorium, so much so that many of the reagents normally used for the determination of thorium have been applied to the determination of zirconium.

Thoron, 1-(o-arsonophenylazo)-2-naphthol-3:6-disulphonic acid, which has become the basis of a colorimetric method for the determination of thorium, has been recently applied to the determination of zirconium (37). Most other colorimetric reagents for the determination of zirconium - alizarin red S (38), chloranilic acid (39), quercetin (40), and p-dimethylaminoazophenylarsonic acid (41) - are subject to the interference of thorium or the rare earth elements, or both, or else are not sufficiently sensitive for analytical application. Alizarin red S has been used for the determination of zirconium in thorium-free magnesium-base alloys by Wengert (42) and by Mayer and Bradshaw (43).

Most of the work that has been done on the analytical chemistry of zirconium has been concerned with organic precipitants such as mandelic acid (44) and its halogen derivatives (45). These reagents are decidedly superior to cupferron (46) and ammonium phosphate (47) as quantitative reagents. The Indian workers, led notably by Raghava Rao, have developed several new organic precipitants for zirconium, e.g., tannin (48), benzilic acid (49) and hydrazine sulphate (50). They have also applied to the determination of zirconium many of the organic precipitants that they developed for the determination of thorium, e.g., fumaric acid (51), salicylic acid, phenoxyacetic acid (52), cinnamic acid (53) and m-cresoxyacetic acid (54).

In order to avoid the ignition that is involved in the gravimetric methods, several volumetric modifications have been devised. White (55) developed a titrimetric method based on the separation of zirconium as the chloro- or bromomandelate. Dhar and Das Gupta (56) have proposed an indirect method in which the zirconium oxalohydromamate precipitate is hydrolyzed to oxalic acid and hydroxylamine and the latter is determined by adding excess titanium(IV) chloride and back titrating with ferrous ion. Kolthoff and Johnson (57) reported an amperometric titration based on precipitation with m-nitrophenylarsonic acid. Fritz and Fulda (58) demonstrated that zirconium can be titrated with ethylenediaminetetracetic acid. Thorium interferes in all these titrimetric methods for zirconium.

Graham _et_. _al_. (59) have proposed the only polarographic method for the determination of zirconium; the method is based on the facts that m-nitrobenzoic acid is a selective precipitant for zirconium and is polarographically reducible. Zirconium is precipitated as zirconium m-nitrobenzoate, the precipitate is washed and dissolved in hydrochloric acid, and the resulting m-nitrobenzoic acid is determined polarographically. The method appears to be applicable to the determination of zirconium in thorium-free magnesium-base alloys.

(iv) Methods for the Separation of Thorium and Zirconium

The usual gravimetric methods for the separation of thorium from the more common ions use either oxalic acid or potassium iodate. Wengert *et. al.* (60), using oxalic acid, have determined thorium in magnesium-base alloys containing zirconium by first separating the thorium and zirconium from the other constituents of the alloy by means of benzoic acid. The benzoate precipitates were dissolved in hydrochloric acid and the thorium precipitated with oxalic acid; the resulting precipitate was ignited to thorium dioxide. The conventional precipitation of thorium with oxalic acid is time consuming because a long digestion period is required for the development of a granular precipitate that can successfully be filtered and washed. A considerable shortening in the time required can be achieved by using the homogeneous precipitation procedure devised by Willard and Gordon (61).

Potassium iodate has often been employed for both the separation and determination of thorium. The thorium iodate has been weighed as such (62), it has been dissolved, reprecipitated as the hydrous oxide and ignited to the oxide (62), or dissolved and titrated with thiosulphate (63), and dissolved and determined polarographically (35). Many difficulties are encountered in an iodate method, especially in the filtration of the thorium iodate in the absence of excess iodate ions; large quantities of this ion are necessary for both the precipitation and washing. Zirconium, if present, is also precipitated as the iodate.

Osborn (64) has reported the separation and gravimetric determination of thorium and zirconium by means of m-nitrobenzoic acid. Venkataramianiah *et. al.* (65) were unable to duplicate this separation.

A separation of titanium, zirconium and thorium by ion exchange using the cationic exchange resin Dowex 50, has been reported by Brown and Rieman (66). The use of cation exchange resins for the separation of the quadrivalent elements requires buffered complexing agents as elutriants. Following the elution, and before any subsequent analytical work can be carried out, these complexing agents usually must be destroyed.

The usual methods of destroying these complexing agents are tedious and time consuming, and, if perchloric acid is used, are inherently dangerous. Acids furnishing anions that complex with thorium and zirconium, such as sulphuric acid, are not desirable as a means to destroy the complexing agents. Accordingly, cationic ion exchange is not attractive as a separational procedure for thorium and zirconium when both elements are to be analytically determined after separation.

Starting about 1949, with the development of such resins as Dowex 1 and Dowex 2, interest in anionic exchange phenomena grew rapidly. By means of anionic exchange, Kraus and Moore (67) have separated zirconium and hafnium in hydrochloric-hydrofluoric acid solutions and Huffman and Lilly (68, 69) have reported the same from hydrochloric acid solutions. Kraus and Moore (70) report an excellent separation of zirconium and niobium in hydrochloric-hydrofluoric acid solutions. Most interesting results on the purification of zirconium, for radiochemical and mass spectrometric studies of neutron deficient zirconium isotopes and their decay products, were reported by Hyde and O'Kelley (71). In this work the zirconium was taken up from 10 M hydrochloric acid on Dowex 1 resin and "milked" periodically for its yttrium daughter activity by rinsing the column with 10-12 M hydrochloric acid. The zirconium is retained quantitatively and the yttrium is quantitatively removed. Using the procedure of Kraus and Moore (70), Melaika (72) has reported a separation of zirconium from fission products and uranium on Dowex 1. Petruska (73) in a fission yield study has reported a separation of plutonium (of an irradiated plutonium-aluminium alloy) from aluminium and fission products in 8 M hydrochloric acid on Dowex 1. After "scavenging" the fission products from the aluminium with an iron(III) hydroxide precipitation, the iron was separated from the fission products by anion exchange.

An anion exchange separation of protactinium from thorium by sorption of the protactinium from 8 M hydrochloric acid has been reported (74); this is based on the fact that thorium does not form negatively charged chloride complexes. The protactinium was subsequently eluted from the column by means of hydrochloric acid of a lower concentration.

Because thorium is not sorbed from hydrochloric or hydrofluoric acid solutions on Dowex 1 resin, whereas zirconium is (71), a separation of the two elements should not present substantial difficulties. The use of hydrofluoric acid is undesirable not only because zirconium and thorium form very stable fluoride complexes which might be expected to complicate further analytical work with the solution but also because of the need for special equipment when working with hydrofluoric acid.

EXPERIMENTAL

In the present research, study has been given to new polarographic methods for thorium, and also some attention has been given to a polarographic method for zirconium. This work is set forth below. Following this, there are described both precipitation and ion exchange methods for separating thorium and zirconium, and procedures for the quantitative separation of these elements when they occur in solutions with compositions corresponding to those of modern magnesium-base alloys.

(A) Apparatus and Materials

(i) Apparatus

All polarographic measurements were carried out at 25.0°C. ± 0.05°C. using a Tinsley pen recording polarograph, type V722/13 (Tinsley Industrial Instruments, London, England). The measurements were made at either 1/20th or 1/50th of the maximum galvanometer sensitivity. The capillary for the dropping mercury electrode was a length of barometer tubing supplied by E. H. Sargent and Company (Chicago, U.S.A.). A conventional "H" type of polarographic cell (75) was used, electrolytic contact to the saturated calomel reference cell being made through a potassium chloride-agar bridge.

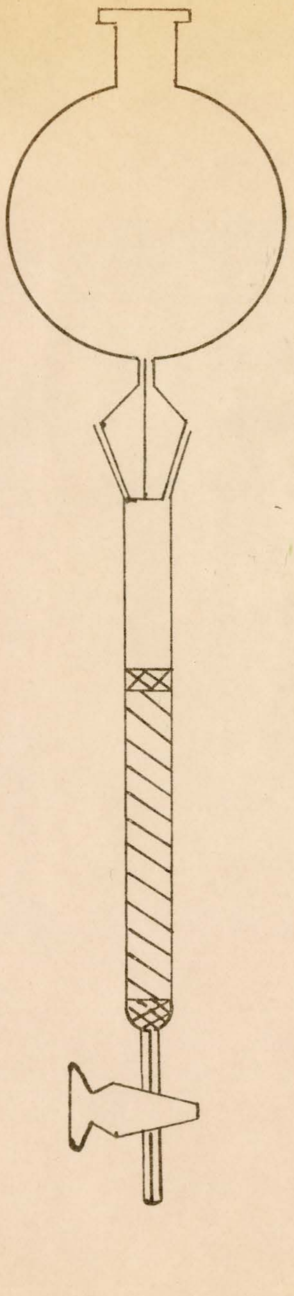
Measurements of pH were made with a Beckman Model G pH meter (Beckman Instruments Inc., South Pasadena, U.S.A.) using a G-1190-80 glass electrode. A Coleman Universal spectrophotometer, model 11 (Coleman Electric Company, Maywood, U.S.A.) was used for the colorimetric measurements.

The construction of the ion exchange columns is shown in Figure I. The resin was Dowex 1, 50-100 mesh, 7.5 percent cross-linkage (Alchem Limited, Burlington, Ontario). It was slurried with water in a beaker, washed into the column, and the particles allowed to settle to form a bed 10 cm. x 0.75 cm^2. The bed was supported at the bottom and kept in place at the top with wads of glass wool. After a resin bed had been formed in the column, it was washed with 25 ml. each of 10 M, 12 M and 4 M hydrochloric acid and then with 25 ml. of water. These washings removed a yellow colour which new resin gives to high concentrations of hydrochloric acid.

(ii) Reagents

Chemical	Grade
Alizarin blue	British Drug Houses, spot test reagent
Alizarin red S	Eastman Kodak, white label
1-(o-arsonophenylazo)-2-naphthol-3:6-disulphonic acid	Eastman Kodak, white label
Benzoic acid	British Drug Houses, Analar
Cacatholine	Eastman Kodak, certified
Dimethyl oxalate	Prepared by the method of Bowden (76) and further purified as described in the Appendix
Gelatin	Eastman Kodak, purified pigskin
Mandelic acid	Eastman Kodak, white label
m-Nitrobenzoic acid	Prepared by the method of Kamm and Sequr (77)

FIGURE I



ION EXCHANGE COLUMN

Chemical	Grade
m-Nitrophenylarsonic acid	Eastman Kodak, white label
n-Propylarsonic acid	Eastman Kodak, white label
8-Quinolinol	British Drug Houses, Analar
Aluminium	Aluminum Company of Canada, Limited
Ceric ammonium nitrate	G. Frederick Smith Company (Columbus, U.S.A.), reference or standard purity
Lanthanum nitrate	British Drug Houses, certified
Hydrochloric acid	Canadian Industries Limited, analyzed grade and stated to contain a minimum of 37% HCl
Hydrogen peroxide	Merck and Company Limited, chemically pure, 30%
Mischmetal	Supplied by Dominion Magnesium Limited and stated to contain: 45 ± 1% cerium, 97% total rare earths, 0.004% thorium, and 3% iron.
Magnesium	Dow Chemical Company (Midland, U.S.A.), sublimed
Mercury	Purified by bubbling for at least ten hours in 10-15% nitric acid, washing several times with water and distilling twice *in vacuo*.
Nitrogen	Purified by bubbling first through a potassium pyrogallate solution and then through distilled water

Chemical	Grade
Thorium tetrachloride	Amend Drug and Chemical Company (New York, U.S.A.), chemically pure and further purified as described in the Appendix
Titaniumtetrachloride	Fisher Scientific Company (Toronto, Ontario), chemically pure
Zirconium oxychloride	Amend Drug and Chemical Company (New York, U.S.A.), chemically pure and further purified as described in the Appendix

All other chemicals were of analyzed grade

(iii) Solutions

A saturated solution of m-nitrobenzoic acid was prepared by dissolving 4 g. of m-nitrobenzoic acid in one liter of hot water, allow- the solution to cool overnight, and filtering off the m-nitro-benzoic acid that had crystallized out.

The 8-quinolinol solution was prepared by dissolving 2.5 g. of 8-quinolinol in 5.7 ml. of 17.5 M acetic acid and diluting to one liter with water.

The gelatin solution was prepared by dispersing 0.75 g. of gelatin in 100 ml. of boiling water and allowing the solution to cool.

(B) Determinations

(i) Thorium

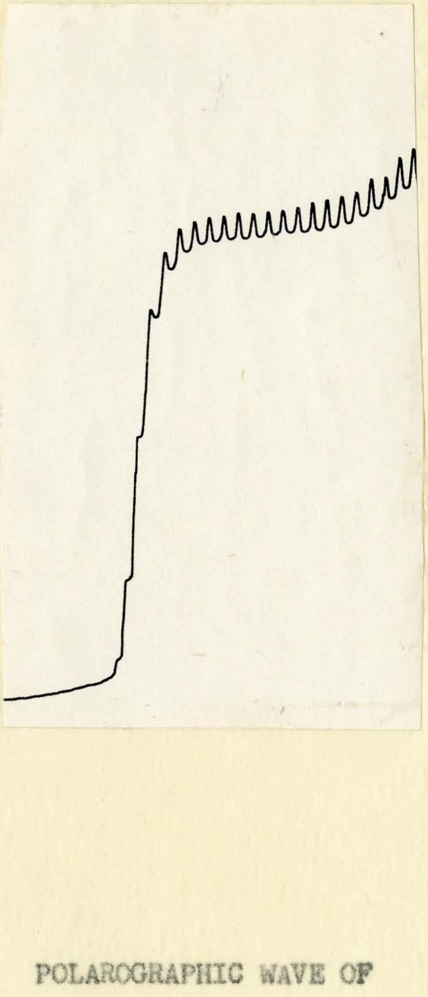
(a) m-Nitrobenzoic Acid

(1) Polarography of m-nitrobenzoic acid: Low concentrations of m-nitrobenzoic acid are easily detected polarographically; the type of wave obtained is shown in Figure II. The height of the wave can easily be measured, with good precision, using the slope-intercept method. The wave shown here, and the ones used throughout this work, correspond to the reduction of the nitro group in a solution buffered at a pH of 4.0 with potassium hydrogen phthalate. Although m-nitrobenzoic acid can give two reduction waves, only one appears at a pH of 4.0; this probably corresponds to a reduction of the nitro group to a phenylhydroxylamine (87).

Because the diffusion current and the half-wave potential of m-nitrobenzoic acid can be expected to vary with pH (79, 80), a good buffer is required to ensure analytically useful results. Potassium hydrogen phthalate serves well both as a buffer and a supporting electrolyte. Although methyl red usually serves as a good maximum suppressor, it was found not to be completely reliable. This was overcome by adding ten drops of a 1% solution of α-naphthol in ethyl alcohol to each 100 ml. of solution before diluting to volume.

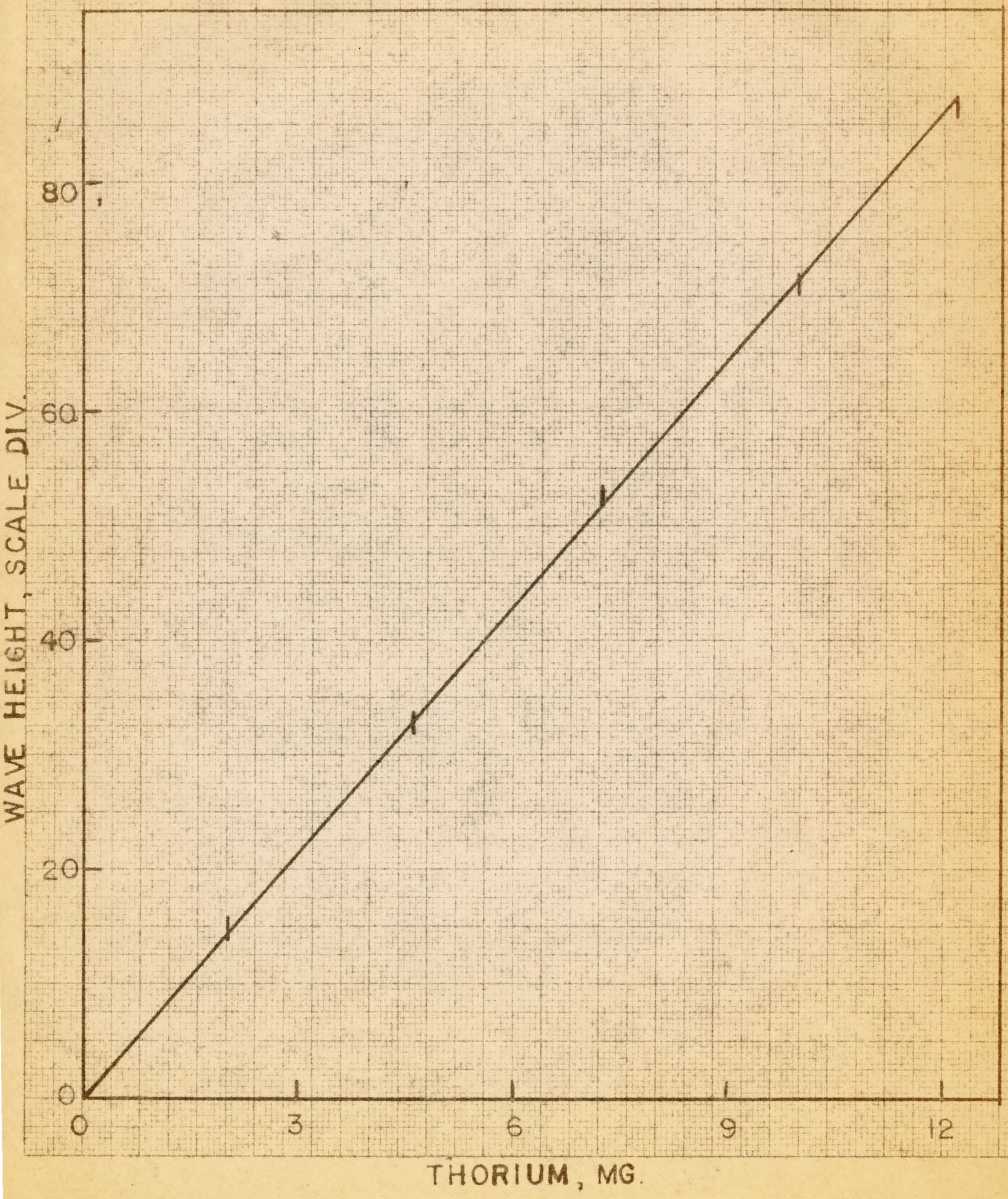
The diffusion current given by m-nitrobenzoic acid is linearly related to the amount of thorium in the original solution, from which both were precipitated, as shown in Figure III. For the construction of this curve, thorium m-nitrobenzoate was precipitated, filtered, and dissolved, and then the free m-nitrobenzoic acid was determined polarographically.

FIGURE II



POLAROGRAPHIC WAVE OF
m-NITROBENZOIC ACID

FIGURE III



(2) Effect of pH on the precipitation of thorium by m-nitrobenzoic acid: An investigation of the effect of pH on the completeness of precipitation of thorium by m-nitrobenzoic acid was carried out. To 50 ml. of a thorium solution containing 10.23 mg. of thorium, there were added 3-4 ml. of 12 M hydrochloric acid and 50 ml. of a saturated aqueous solution of m-nitrobenzoic acid. A mechanical stirrer and the electrodes of a pH meter were placed in the solution, and then the thorium was precipitated by adjusting the pH, using 7.5 M ammonia. The precipitate was coagulated by heating the mixture near the boiling point for about 15 minutes, and then was filtered on Whatman #40 filter paper. Next the precipitate was carefully washed with hot water and dissolved directly into a 100 ml. volumetric flask using hot perchloric acid solution (one volume of 72% perchloric acid to two volumes of water). Five ml. of a 20% tartaric acid solution were added and the solution was neutralized to the methyl red end point by adding 15 M ammonia from a burette. Thirty-five ml. of a saturated potassium hydrogen phthalate solution and 10 drops of a 1% solution of α-naphthol in ethyl alcohol were added and the solution made up to the mark with water. A portion was decanted into a polarographic cell, bubbled with purified nitrogen for ten minutes, and then polarographed.

A plot of the average height of five waves given by m-nitrobenzoic acid versus the pH of precipitation is shown in Figure IV. Clearly the acidity for precipitation is fairly critical; only over a narrow range of pH values does the precipitate have a constant composition. From hydrochloric acid solutions thorium gives no precipitate below pH 1.7, and a precipitate of constant composition from pH 1.8 to 2.5. At pH

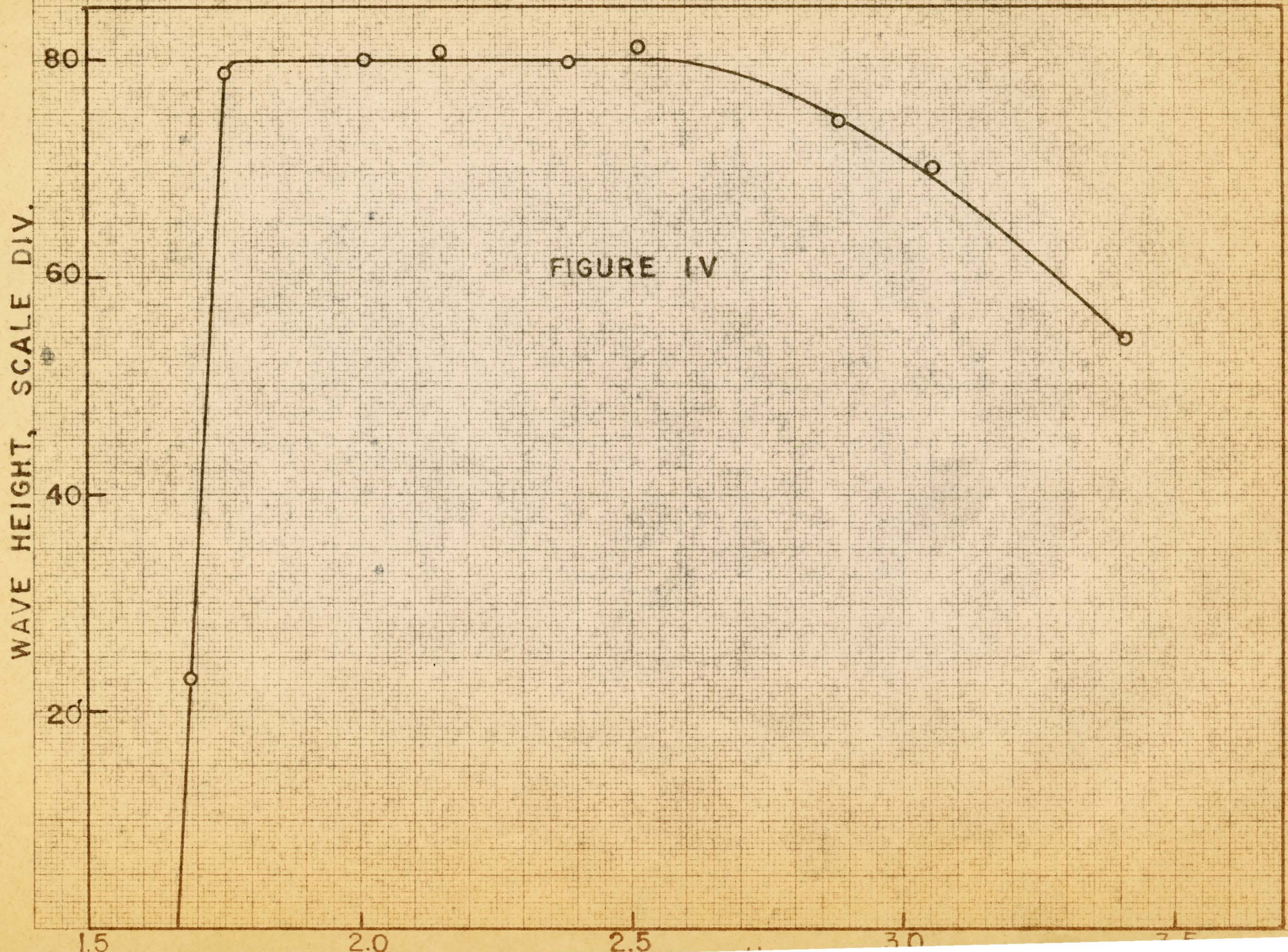


FIGURE IV

values greater than 2.5, a mixture (of the m-nitrobenzoate and the hydrous oxide of thorium in all probability) is apparently obtained. A pH value of 2.05 to 2.25 for the precipitation is best, at least with the concentrations of reagents used in these experiments.

(3) Notes on the m-nitrobenzoate procedure: The experiments described above show that the pH range for the useful precipitation of thorium m-nitrobenzoate, under the conditions and concentrations used, is 2.15 ± 0.30. This range of pH values is not unduly restrictive. It is considered best, however, that the safer range, 2.15 ± 0.10 be used.

It was found that the precipitated thorium m-nitrobenzoate was only moderately soluble in hot 7.5 M nitric acid, 12 M hydrochloric acid, and 9 M sulphuric acid. Higher concentrations of these acids were not desirable because they caused pieces of filter paper to collect in the volumetric flask, making polarography difficult. A hot perchloric acid solution (one volume of 72% perchloric acid to two volumes of water, or about 4 M) was found to dissolve the precipitate rapidly and efficiently.

After the thorium m-nitrobenzoate had been dissolved, it was found necessary to complex the thorium so that subsequent manipulation of pH, in preparing the solution for polarography, would not cause reprecipitation of the thorium as the m-nitrobenzoate. Tartaric acid proved to be an effective complexing agent.

(4) Procedure for polarographically determining thorium as the m-nitrobenzoate: To the thorium solution, diluted to 50 ml., and containing about 10 mg. of thorium, are added 50 ml. of a saturated m-nitrobenzoic

acid solution. The thorium m-nitrobenzoate is precipitated by adjusting the pH of the solution to 2.15 ± 0.10 using 7.5 M ammonia. During the adjustment, the pH is measured with a pH meter. The precipitate is coagulated by heating the mixture near the boiling point for about 15 minutes, and is filtered through Whatman #40 filter paper. The precipitate is carefully washed with hot water and then dissolved directly into a 100 ml. volumetric flask using hot perchloric acid solution (one volume of 72% perchloric acid to two volumes of water). Five ml. of 20% tartaric acid solution are added and the solution is neutralized to the methyl red end point by adding 15 M ammonia from a burette. Thirty-five ml. of a saturated potassium hydrogen phthalate solution and 10 drops of a 1% solution of α-naphthol in ethyl alcohol are added and the solution is made up to the mark with water. A portion of the solution is decanted into a polarographic cell, bubbled with nitrogen for ten minutes, and then polarographed.

The average height of five waves for the reduction step of m-nitrobenzoic acid is taken and the corresponding concentration of thorium is assessed by reference to a calibration curve (Figure III). The calibration curve is prepared in a similar manner, with solutions of known thorium content. The calibration solutions were prepared by dissolving purified thorium tetrachloride in 5% hydrochloric acid, and the thorium content was determined by precipitation of the hydrous oxide using ammonia, followed by ignition to thorium dioxide.

(5) Interferences in the m-nitrobenzoate method: In a study of the procedure for the precipitation of thorium by means of m-nitrobenzoic acid as proposed by Neish (81), Osborn (64) confirmed Neish's observations

that zirconium, hafnium, titanium and cerium(IV) are also precipitated, and that tin(II), tin(IV), mercury(I) and mercury(II) interfere because of hydrolysis effects. m-Nitrobenzoic acid will precipitate plutonium(IV) but plutonium, like cerium, will not precipitate when it is reduced to the (III) state (64, 97).

Crepaz and Marchesini (82) have reported that when the pH of an iron(III) solution is adjusted to 1.0 - 1.5, m-nitrobenzoic acid and the m-nitrobenzoates of sodium and ammonium yield a precipitate of iron(III) m-nitrobenzoate. They also reported that under similar conditions for the precipitation of iron(III), sodium m-nitrobenzoate will precipitate chromium, thorium, bismuth, copper, lead, mercury, aluminium, titanium, tin, barium, uranium, cerium(IV), yttrium and zirconium, and that a separation of iron(III) from these elements could not be obtained.

It was found that under the conditions for the precipitation of thorium as developed in the present study, up to 40 mg. of copper, lead, aluminium, lanthanum, and barium in 50 ml. of solution, did not yield polarographically reducible precipitates from hydrochloric acid solutions. Also, from hydrochloric acid solutions containing up to 70 mg. of mischmetal in 50 ml. of solution, no polarographically reducible precipitates could be obtained under the conditions used for the thorium determination. Further, at pH values up to 8.0, none of these elements gave precipitates that yielded polarographically reducible substances.

From these experiments it would appear that the work of Crepaz and Marchesini (82) is not relevant to the present study. The elements most likely to interfere in this procedure are zirconium, hafnium, titanium, tin(II), tin(IV), mercury(I), and mercury(II).

A procedure for the determination of thorium using m-nitrobenzoic acid, taking account of the possible interfering elements in magnesium-base alloys, is given later, in Sections D(a) and D(b).

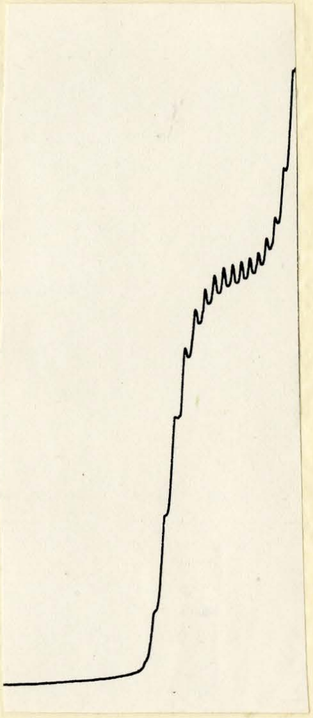
(b) 8-Quinolinol

<u>(1) Polarography of 8-quinolinol</u>: The behaviour of 8-quinolinol at the dropping mercury electrode is, in general, complicated and strongly dependent on pH (83). The reduction of 8-quinolinol in alkaline medium is, however, simple and reversible (84). Although 8-quinolinol can give two reduction waves in alkaline solution, only one wave is obtained at pH 12; the type of wave obtained is shown in Figure V. The wave probably corresponds to the reduction of the 8-quinolinol to the dihydro compound (78). The height of the wave can be measured with good precision by the slope-intercept method.

Because the diffusion current and the half-wave potential of 8-quinolinol are dependent upon pH (83), a good buffer is required to ensure analytically useful results. A solution of di sodium monohydrogen phosphate (0.1 M) and sodium hydroxide (0.1 M) of pH 12 can serve both as a buffer and a supporting electrolyte. The use of gelatin eliminates all maxima at this pH.

The diffusion current given by the 8-quinolinol resulting from the dissolution of thorium 8-quinolinate is linearly related to the amount of thorium in the original solution. This is shown in Figure VI. Figure VII is another calibration curve, obtained not by dissolving the precipitated thorium 8-quinolinate (as for Figure VI), but by determining the excess 8-quinolinol remaining in solution after the addition of constant amounts of 8-quinolinol to solutions of known thorium content.

FIGURE V



POLAROGRAPHIC WAVE OF

8-QUINOLINOL

FIGURE VI

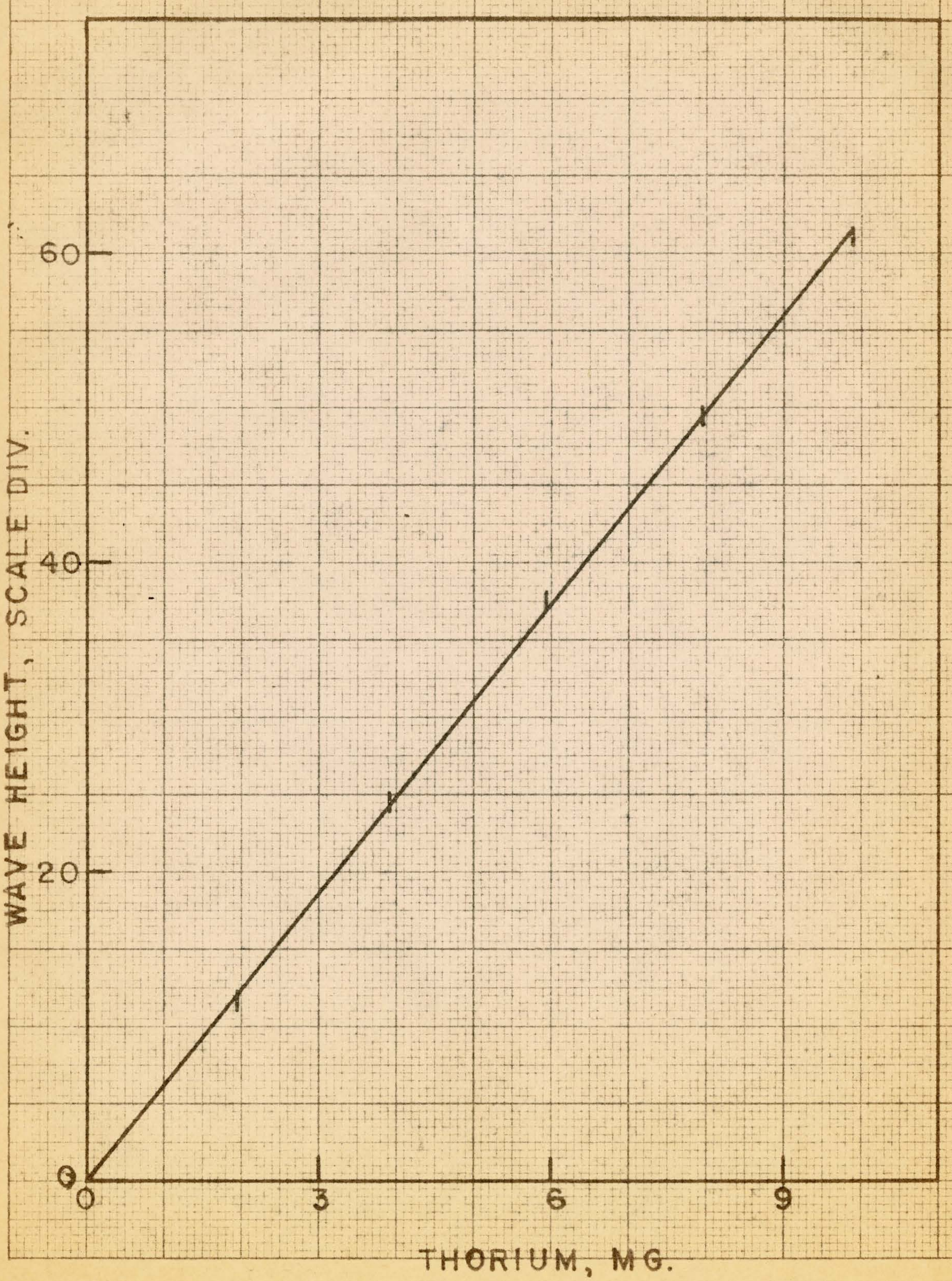
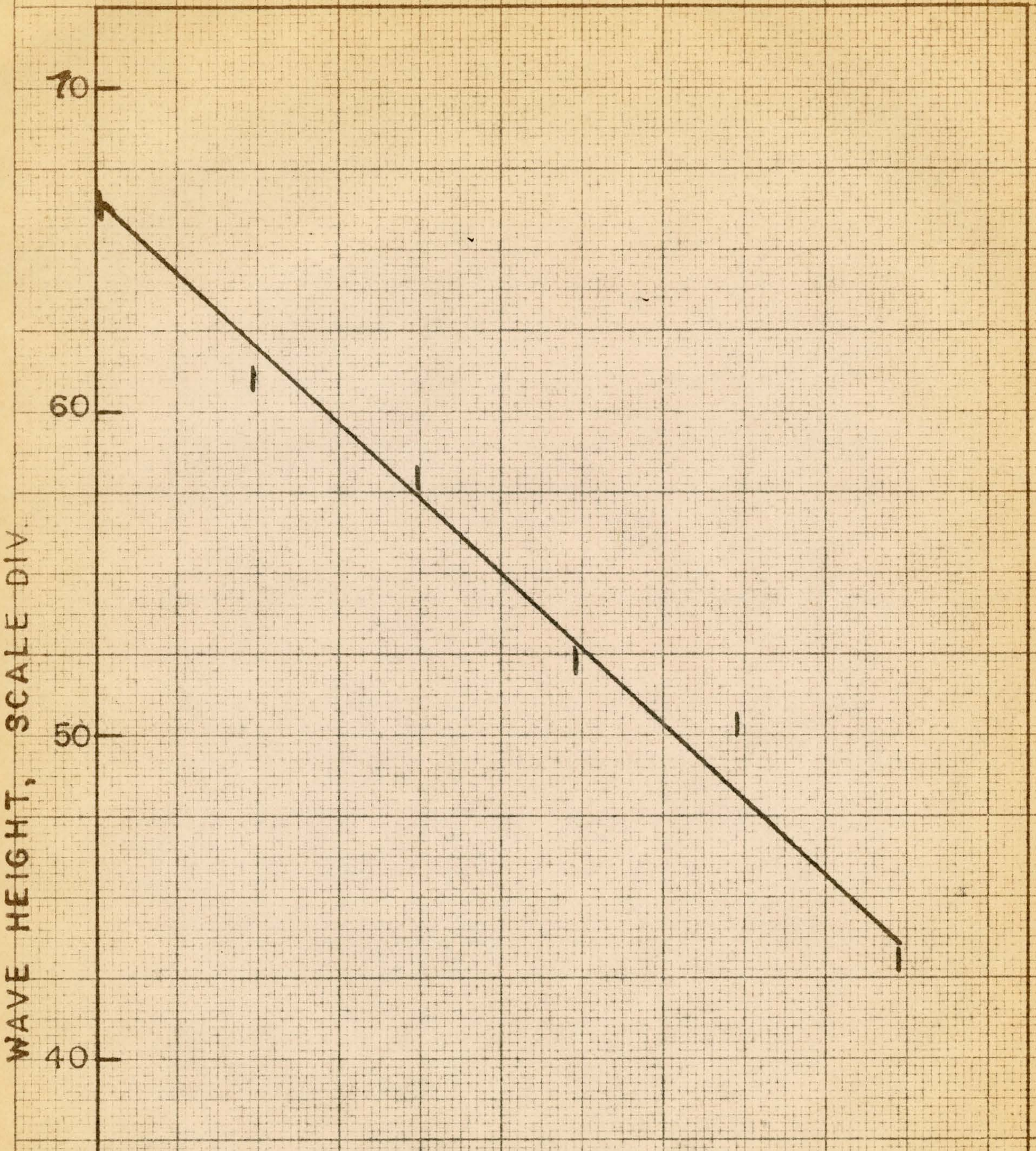


FIGURE VII



Use of these two linear relationships was made in the development of polarographic methods for the determination of thorium with 8-quinolinol.

(2) Notes on the 8-quinolinate procedures: In this work it was found that moderate amounts of ammonium ion hinder the hydrolysis of urea, and therefore ammonia should be avoided as much as possible in any neutralizations prior to the hydrolysis of the urea used in the homogeneous precipitation of thorium 8-quinolinate.

Thorium 8-quinolinate dissolves readily in all the common acids. Acids furnishing anions that discharge at a potential close to that of 8-quinolinol, such as nitric acid, should be avoided because of their masking effect on the wave. A rapid, efficient dissolution of the thorium 8-quinolinate can easily be effected with hot 6 M hydrochloric acid.

In what follows in (3) and (4) below, a method based on a calibration curve such as that of Figure VI, obtained by dissolving a precipitate of thorium 8-quinolinate, is called a "direct" procedure, and one based on a calibration curve such as that of Figure VII, obtained by determining the excess 8-quinolinol in the solution, is called an "indirect" procedure.

(3) "Direct" 8-quinolinol procedure: To 50 ml. of a thorium solution containing about 10 mg. of thorium is added 8 M sodium hydroxide dropwise until hydrous oxide just succeeds in redissolving on stirring, and then 10 ml. of a 2.5% acetic acid solution of 8-quinolinol and 12 g. of urea are added. The solution is kept just below the boiling point until the orange-red precipitate, which slowly forms on hydrolysis of the urea, coagulates. The precipitate is filtered on Whatman

#42 filter paper and washed thoroughly with water. The thorium 8-quinolinate precipitate is dissolved directly into a 100 ml. volumetric flask using hot 6 M hydrochloric acid. Five ml. of 20% tartaric acid solution are then added and the solution adjusted to the alizarin blue end point with 8 M sodium hydroxide. Two more ml. of 8 M sodium hydroxide, 35 ml. of disodium monohydrogen phosphate (0.1 M) and sodium hydroxide (0.1 M) buffer solution of pH 12.0, and 1 ml. of 0.75% gelatin are added, and the solution is made up to the mark with water. A portion of the solution is decanted into a polarographic cell, bubbled with purified nitrogen for ten minutes, and then polarographed.

The average height of five waves for the reduction step of 8-quinolinol is taken and the corresponding concentration of thorium assessed by reference to a calibration curve. The calibration curve was prepared by similar measurements made in the same way, with solutions of known thorium content. Such solutions were prepared by dissolving purified thorium tetrachloride in 5% hydrochloric acid; the thorium content was determined by precipitation of the hydrous oxide using ammonia, followed by ignition to thorium dioxide.

<u>(4) "Indirect" 8-quinolinol procedure:</u> The procedure for the precipitation of the thorium is identical to that given above under (3) except that exactly 10.00 ml. of 8-quinolinol solution are added by pipette before the urea is added. After coagulation of the precipitate as before, it is filtered on Whatman #42 filter paper and the filtrate and washings are caught in a 250 ml. volumetric flask. The filtrate is adjusted to the alizarin blue end point with 8 M sodium hydroxide and 5 ml. more of sodium hydroxide are added. Fifty ml. of disodium monohydrogen phosphate

(0.1 M) and sodium hydroxide (0.1 M) buffer solution of pH 12.0, and 2.5 ml. of 0.75% gelatin solution are added, and the solution is made up to the mark with water. A portion of the solution is decanted into a polarographic cell, bubbled with purified nitrogen for ten minutes, and then polarographed.

As before, the average height of five waves for the reduction step of 8-quinolinol is taken and the corresponding concentration of thorium assessed by reference to a calibration curve. The calibration curve was prepared by similar measurements made in the same way, with solutions of known thorium content, determined as before.

(5) Comparison of 8-quinolinate precipitation methods: The homogeneous precipitation of thorium 8-quinolinate with urea has all the advantages inherent in any homogeneous precipitation. The precipitate coagulates rapidly, has little tendency to creep, and is easily filtered. In contrast, the precipitation of thorium by the classical methods (85, 86) yields a bulky precipitate that is slow to coagulate, creeps badly, sticks to the sides of the beaker, and is difficult to filter.

From photomicrographs of the precipitates the reason for the difference in the physical properties becomes apparent. In the homogeneous precipitation (Figure VIII) there are formed little worm-like crystals which are easily washed and filtered. Figure IX shows a thorium 8-quinolinate precipitate obtained by the method of Frere (86). The long needle-like crystals obtained by this method suggest in their arrangement a brush heap. These do not pack easily and the agglomeration is not readily washed free of contaminating mother liquor.

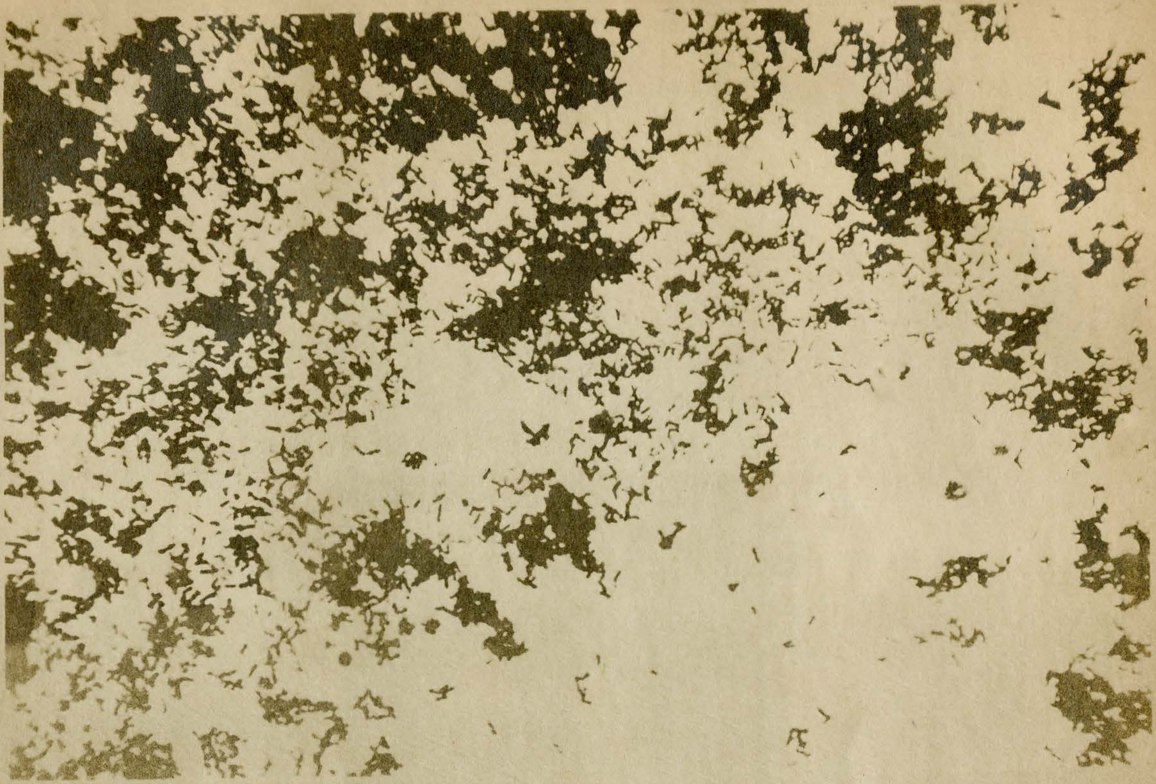


FIGURE VIII

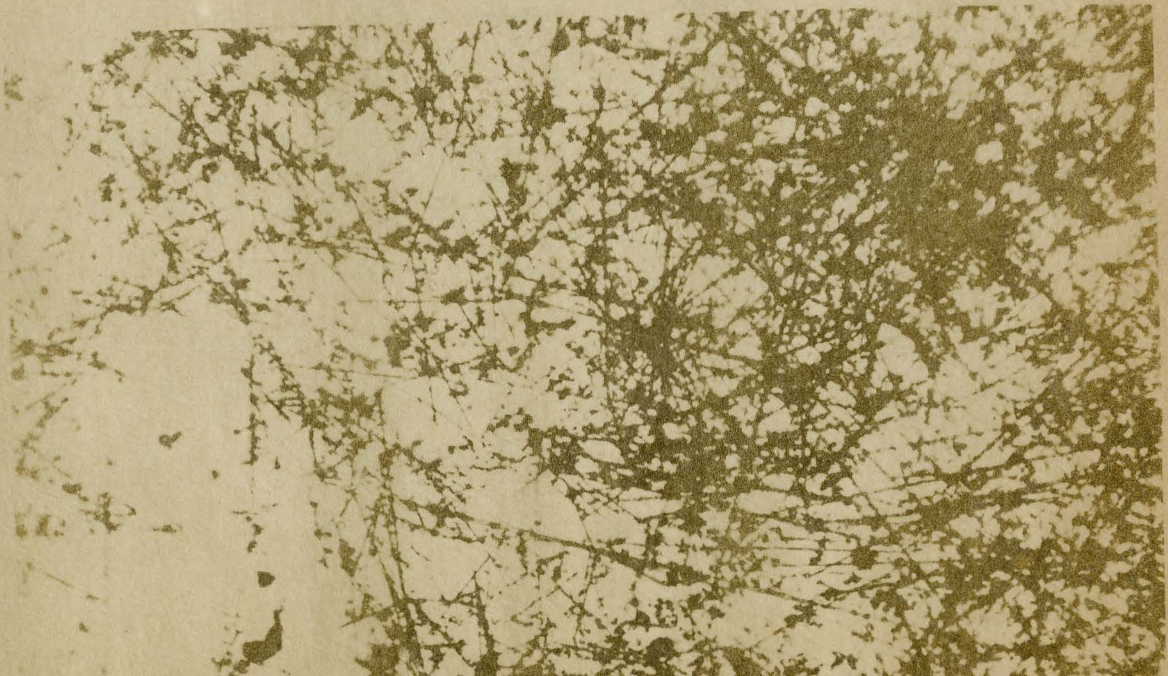


FIGURE IX

(c) m-Nitrophenylarsonic Acid

(1) Polarography of m-nitrophenylarsonic acid: Although m-nitrophenylarsonic acid can give three polarographic reduction waves, only one appears at a pH of 4.0; this probably corresponds to a reduction of the nitro group to a phenylhydroxylamine (87). The type of wave given by m-nitrophenylarsonic acid at this pH is shown in Figure X. The height of the wave can easily be measured with good precision using the slope-intercept method. The wave corresponds to the reduction of the nitro group at the dropping mercury electrode in a solution buffered at a pH of 4.0 with potassium hydrogen phthalate.

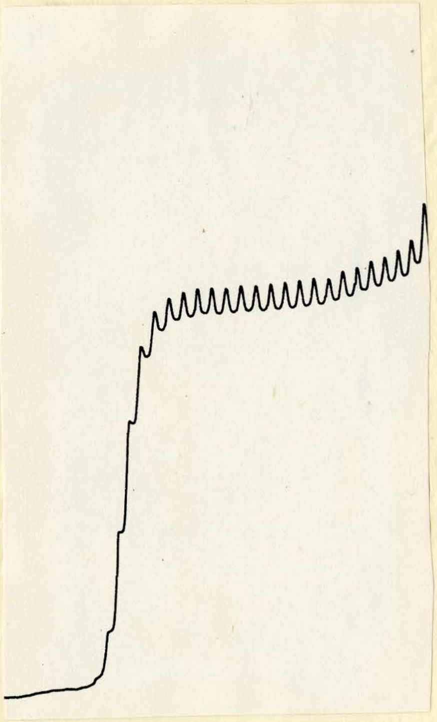
Because the diffusion current given by m-nitrophenylarsonic acid can be expected to vary with pH (87), a good buffer is required as with m-nitrobenzoic acid and 8-quinolinol. It has been found in this laboratory that potassium hydrogen phthalate serves well both as a buffer and a supporting electrolyte. Methyl red, which is present in this procedure, serves well as a maximum suppressor.

The diffusion current given by m-nitrophenylarsonic acid is linearly related to the amount of thorium in the solution, from which both were precipitated, as shown in Figure XI. For the construction of the curve, thorium m-nitrophenylarsonate was precipitated, filtered, dissolved and the free m-nitrophenylarsonic acid was determined polarographically.

(2) Effect of pH on the precipitation of thorium by m-nitrophenylarsonic acid: An investigation was made of the effect of pH on the completeness of precipitation of thorium by m-nitrophenylarsonic acid.

To 50 ml. of the thorium solution containing about 10 mg. of thorium, there was added 3 M hydrochloric acid or 4 M ammonia until the pH desired

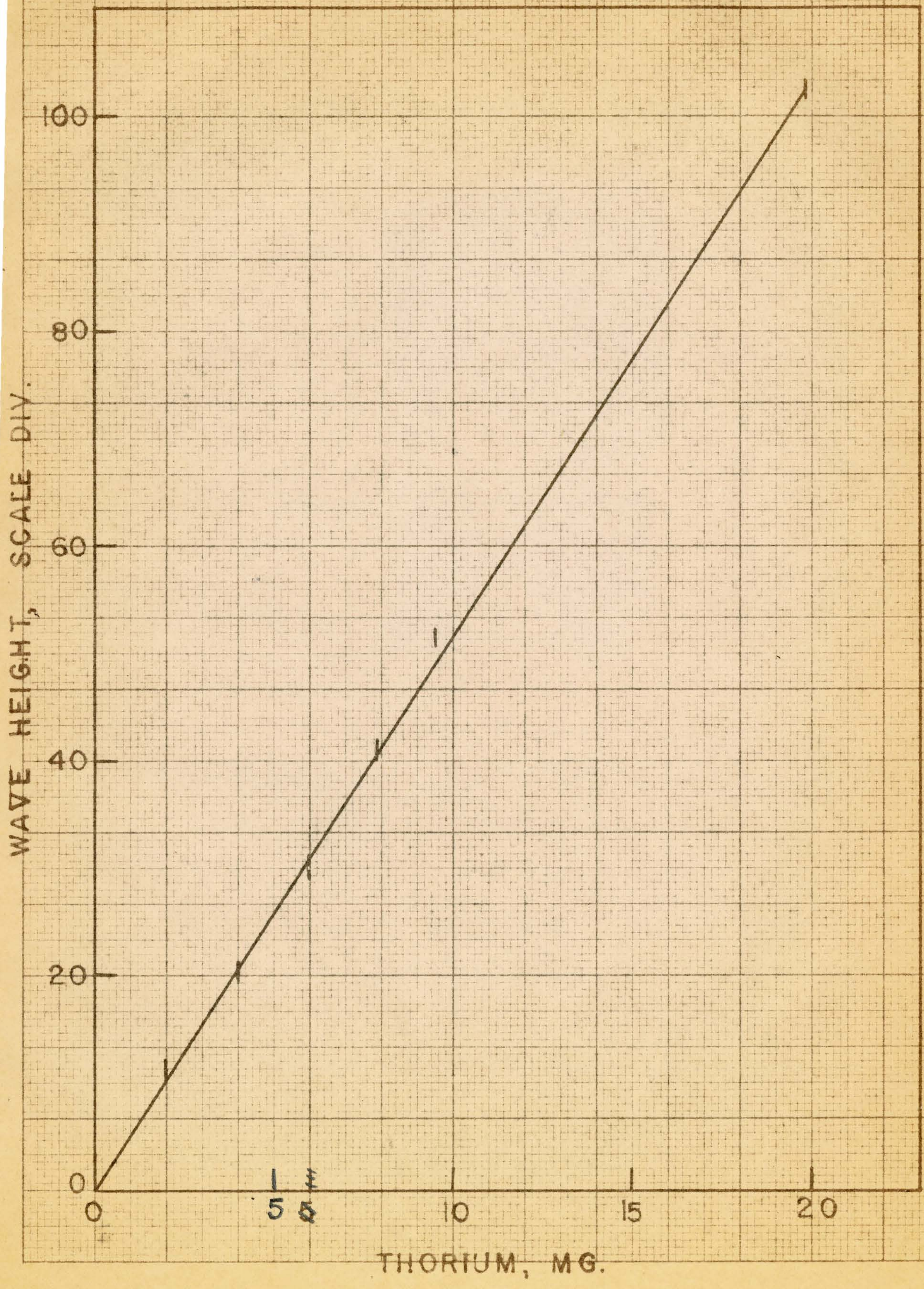
FIGURE X



POLAROGRAPHIC WAVE OF

m-NITROPHENYLARSONIC ACID

FIGURE XI



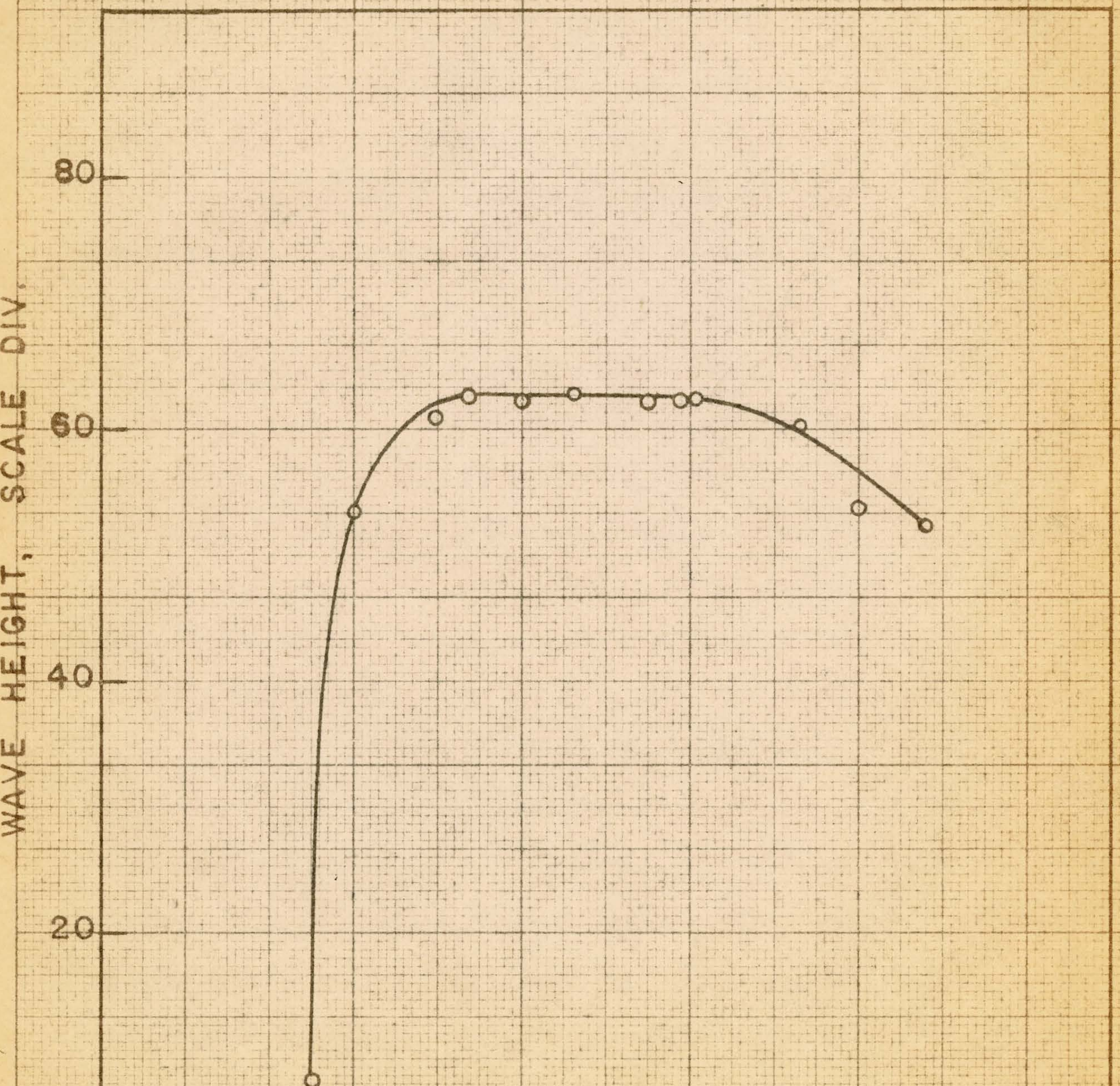
for precipitation was obtained. The thorium was precipitated by adding 50 ml. of a solution, of the same pH, containing 15 ml. of 0.08% aqueous m-nitrophenylarsonic solution. The precipitate was kept at room temperature for two hours to coagulate it, then filtered on Whatman #42 filter paper, and then washed four times with water. Next, the precipitate was dissolved directly into a 100 ml. volumetric flask with a hot saturated sodium tartarate solution made strongly alkaline with sodium hydroxide, and the solution was adjusted to the methyl red point using 5 M perchloric acid. Thirty-five ml. of saturated potassium hydrogen phthalate solution were added and the solution diluted to volume with water. A portion of the solution was decanted into a polarographic cell, bubbled with purified nitrogen for ten minutes, and polarographed.

A plot of the average height of five waves given by m-nitrophenylarsonic acid versus the pH of precipitation is shown in Figure XII. The pH conditions for precipitation are rather critical; only over a narrow range of pH values is the precipitate of constant composition. From hydrochloric acid solutions, thorium gives no precipitate below a pH of 0.7, and a precipitate of constant composition over the pH range 1.5 to 2.7. A pH value of 2.0 for the precipitation is best, at least with the concentrations of reagents used in these experiments.

(3) Notes on the m-nitrophenylarsonate procedure: The experiments described above show that the optimum pH range for the precipitation of thorium by m-nitrophenylarsonic acid is 2.0 ± 0.1. Although quantitative precipitation could be obtained over a wider pH range, it is felt that it is safer to restrict the pH range to these values.

The precipitation of thorium m-nitrophenylarsonate dissolves readily

FIGURE XII



in a hot saturated sodium tartarate solution made strongly alkaline with sodium hydroxide.

(4) Procedure for polarographically determining thorium by means of m-nitrophenylarsonic acid: To 50 ml. of a thorium solution containing about 10 mg. of thorium is added 3 M hydrochloric acid or 4 M ammonia until the pH of the solution is 2.0 ± 0.1. The thorium is precipitated by adding 50 ml. of a solution at pH 2.0 containing 15 ml. of aqueous 0.08% m-nitrophenylarsonic acid solution. The mixture is coagulated by keeping the solution at room temperature for two hours. The precipitate is filtered on Whatman #42 filter paper, washed four times with water, and then dissolved directly into a 100 ml. volumetric flask by means of a hot saturated sodium tartarate solution made strongly alkaline with sodium hydroxide. The solution is adjusted to the methyl red end point with 5 M perchloric acid. Thirty-five ml. of saturated potassium hydrogen phthalate solution are added and the solution diluted to volume with water. A portion of the solution is decanted into a polarographic cell, bubbled with purified nitrogen for ten minutes, and then polarographed.

The average height of five waves for the reduction step of m-nitrophenylarsonic acid is taken and the corresponding concentration of thorium is assessed by reference to a calibration curve (Figure XI). The calibration curve is prepared in a similar manner, with solutions of known thorium content. The calibration solutions were prepared by dissolving purified thorium tetrachloride in 5% hydrochloric acid, and the thorium content was determined by precipitation of the hydrous oxide using ammonia, followed by ignition to thorium dioxide.

(ii) Zirconium

(a) m-Nitrobenzoic Acid

(1) Effect of pH and amount of reagent: The effect of pH on the precipitation of zirconium by m-nitrobenzoic acid was studied by precipitating a constant amount of zirconium with a constant amount of m-nitrobenzoic acid, at various pH values.

To 50 ml. of a solution containing 15.2 mg. of zirconium were added 50 ml. of a saturated m-nitrobenzoic acid solution, and then a mechanical stirrer and the electrodes of a pH meter were introduced into the solution. The pH was adjusted with 7.5 M ammonia and the precipitate which formed was coagulated by heating the mixture near the boiling point for about thirty minutes. The precipitate was then filtered on Whatman #40 filter paper, carefully washed with hot water, and then dissolved directly into a 100 ml. volumetric flask with hot 6 M sulphuric acid. Five ml. of a 20% tartaric acid solution were added and the solution was adjusted to the methyl red end point with 15 M ammonia. Thirty-five ml. of a saturated potassium hydrogen phthalate solution and 10 drops of a 1% solution of α-naphthol in ethyl alcohol were added and the solution made up to the mark with water. A portion was decanted into a polarographic cell, bubbled with purified nitrogen for ten minutes, and polarographed.

A plot of the average height of five waves versus the pH of precipitation indicated that the best pH for the precipitation of zirconium using 50 ml. of saturated m-nitrobenzoic acid was about 0.65.

An investigation into the effect of the amount of reagent on the precipitation of zirconium by m-nitrobenzoic acid was made by precipitating a constant amount of zirconium at a constant pH of 0.65 with various amounts of m-nitrobenzoic acid.

To 50 ml. of a solution containing 15.2 mg. of zirconium there was added a measured amount of saturated m-nitrobenzoic acid solution, and then a mechanical stirrer and the electrodes of a pH meter were introduced into the solution as before. The pH was adjusted to 0.65 with 7.5 M ammonia and the precipitated zirconium m-nitrobenzoate was coagulated, filtered, dissolved and the solution polarographed as before.

It was found that as the amount of saturated m-nitrobenzoic acid solution increased from 50 to 200 ml., the wave height increased by as much as 27%. The experiment was repeated using a substantially larger amount of m-nitrobenzoic acid. One hundred ml. of hot 1% m-nitrobenzoic acid solution (adjusted beforehand to pH 0.65 with 12 M hydrochloric acid) were added to the zirconium solution, also heated to the boil. The precipitated zirconium m-nitrobenzoate was coagulated, filtered, washed, dissolved and polarographed, as before.

In these experiments a further increase in wave height was obtained, with the results of triplicate experiments being in very good agreement (64.2 ± 0.1; 64.1 ± 0.1; 63.8 ± 0.3).

In order to ascertain if there was any change in the optimum pH for precipitation with this large excess of m-nitrobenzoic acid, another series of experiments relating pH of precipitation to wave height was carried out. The pH of the 50 ml. of solution containing 15.2 mg. of zirconium was adjusted to the desired pH with 7.5 M ammonia or 6 M hydrochloric acid. The 100 ml. of 1% aqueous m-nitrobenzoic acid solution was adjusted to the same pH with 12 M hydrochloric acid, and both solutions heated to boiling before being brought together. The precipitated zirconium m-nitrobenzoate was coagulated, filtered, washed, dissolved and the solution polarographed, as before.

It was found that a constant wave height was obtained from pH 0.35 to 0.85.

(2) Effect of concentration of zirconium: It was found that a smooth but not linear calibration curve was obtained if less than 3 mg. of zirconium per 100 ml. of solution were precipitated. As shown in Figure XIII, however, a good straight-line calibration curve was obtained when from 3 to 15.1 mg. of zirconium were precipitated.

(3) Notes on the procedure: The best pH for the precipitation of about 10 mg. of zirconium with m-nitrobenzoic acid is about 0.65, and no difficulty is encountered in controlling the pH to such a value.

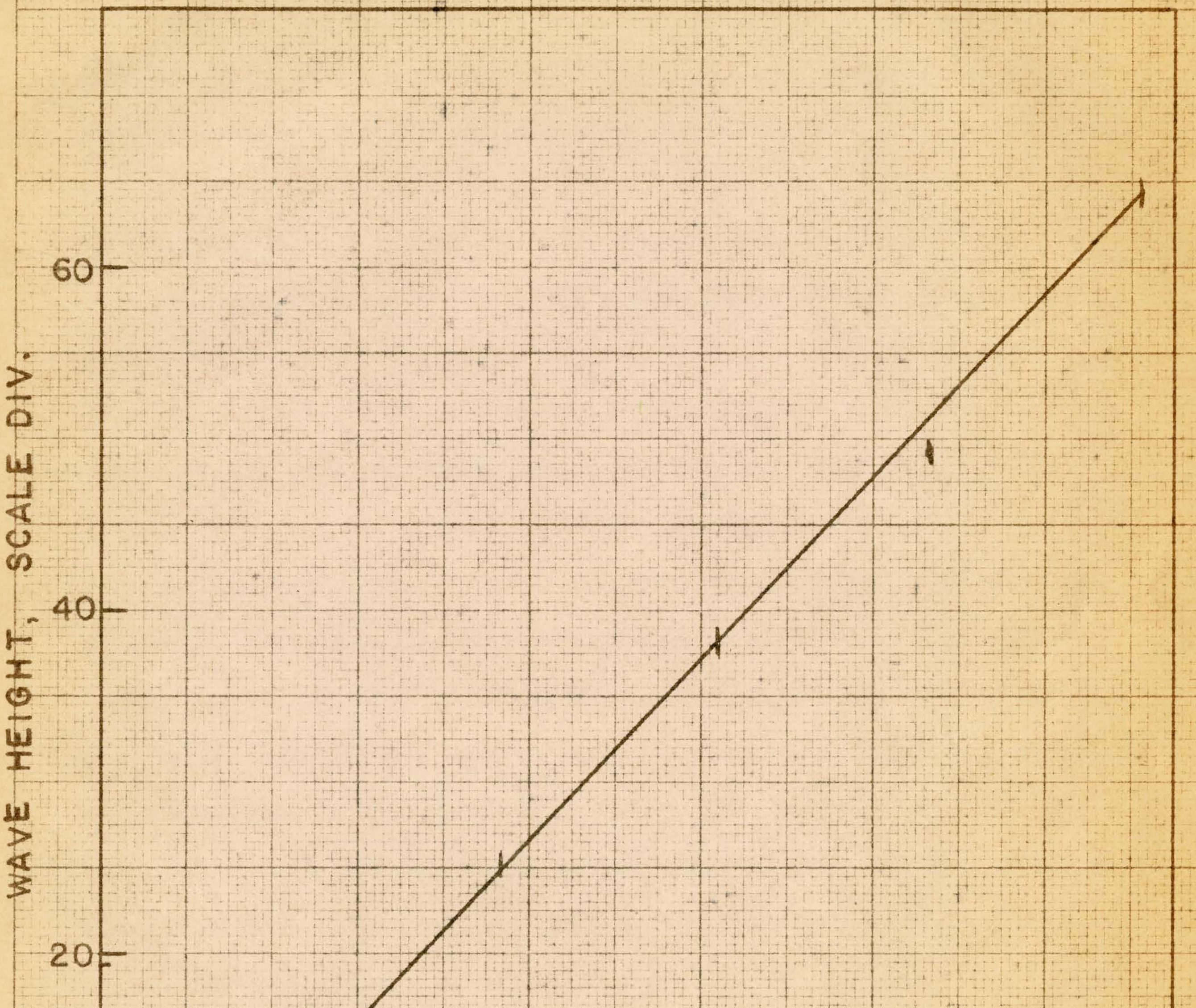
As indicated above, a large excess of m-nitrobenzoic acid is necessary to obtain an analytically useful precipitate of zirconium with this reagent. These experiments indicated that at least a 36-fold excess of m-nitrobenzoic acid is necessary.

The precipitate was found to be very soluble in 6 M sulphuric acid but not appreciably soluble in moderate concentrations of other common acids.

With these considerations in mind, the following procedure for the determination of zirconium with m-nitrobenzoic acid is suggested.

(4) Procedure for the determination of zirconium with m-nitrobenzoic acid: The pH of the zirconium solution, containing about 10 mg. of zirconium and diluted to about 50 ml., is adjusted to 0.65 ± 0.10 with 7.5 M ammonia, with the measurement made on a pH meter. In a similar manner, the pH of 100 ml. of water containing 1 g. of m-nitrobenzoic acid is

FIGURE XIII



adjusted to 0.65 ± 0.1 using 6 M hydrochloric acid. Both solutions are heated to boiling and the zirconium is precipitated by adding the hot m-nitrobenzoic acid solution to the zirconium solution. The precipitate is coagulated by heating the mixture near the boiling point for thirty minutes, and then is filtered on Whatman #40 filter paper. The precipitate is carefully washed with hot water and dissolved directly into a 100 ml. volumetric flask with hot 6 M sulphuric acid. Five ml. of 20% tartaric acid are added and the solution is adjusted to the methyl red end point using 15 M ammonia. Thirty-five ml. of saturated potassium hydrogen phthalate solution and 10 drops of a 1% solution of α-naphthol in ethyl alcohol are added and the solution is diluted to the mark with water. A portion is decanted into a polarographic cell, bubbled with purified nitrogen for ten minutes, and then polarographed.

The average height of five waves for the reduction step of m-nitrobenzoic acid is taken and the corresponding concentration of zirconium is assessed by reference to a calibration curve (Figure XIII). The calibration curve is prepared in a similar manner, using solutions of known zirconium content. The calibration solutions were prepared by dissolving zirconium oxychloride in 5% hydrochloric acid, and the zirconium content determined by precipitation of the hydrous oxide using ammonia, followed by ignition to zirconium dioxide.

(C) Separations

The determination of thorium in the presence of zirconium, as is necessary in certain magnesium-base alloys, is extremely difficult unless a preliminary separation is carried out. A number of separations using organic precipitants were studied (Section (a) below), but these were found not to be as successful as an anion exchange separation (Section (b) below).

(i) By Precipitation

(a) Benzoic Acid

Owing to the large excess of magnesium in magnesium-base alloys, a preliminary separation of the thorium and zirconium from the other elements present was carried out, making use of benzoic acid (88).

Ten grams of ammonium chloride were added to a solution of the alloy, and the pH was adjusted to 2.4 ± 0.2, making use of a pH meter. The thorium and zirconium were precipitated by adding 100 ml. of a hot 2% aqueous benzoic acid solution, and the mixed benzoate precipitate was coagulated by heating and then filtered on Whatman #41H filter paper. The precipitate was carefully washed with water and dissolved into a 250 ml. beaker with hot 12 M hydrochloric acid.

It was from the solution of this dissolved precipitate that the separations with mandelic acid, n-propylarsonic acid and dimethyl oxalate ((1) to (3), below) were attempted. Following such separations the thorium could be determined by a polarographic method.

<u>(1) Mandelic acid</u>: The use of mandelic acid to separate thorium and zirconium, according to the procedure of Hahn (44), was investigated.

To a 10% hydrochloric acid solution of the thorium and zirconium were added 50 ml. of a 16% mandelic acid solution, which precipitated the zirconium as the mandelate. The precipitate was coagulated at 85°C., filtered on Whatman #41H filter paper, and washed six to eight times with hot water. The precipitate was dried and then ignited. The results obtained were:

Zirconium added, as ZrO_2: 0.0570 ± 0.0002 g.
Zirconium recovered, as ZrO_2: 0.0565 g.
0.0566 g.
0.0571 g.
Average: 0.0567 ± 0.0003 g.

It would appear from these data that a reasonably good separation of zirconium from thorium can be effected with mandelic acid.

When an attempt was made to precipitate the thorium in the filtrate with 8-quinolinol, no precipitate was obtained. Further, it was found that, in the presence of mandelic acid, thorium could not be precipitated as the hydrous oxide. Presumably the mandelic acid had reacted with the thorium to yield a very stable complex.

An attempt was made to destroy the mandelic acid with potassium permanganate but an end point in the titration could not be obtained due to the presence of hot chloride ion. In order to dispose of chloride ion, a mandelic acid separation of the thorium and zirconium was carried out under similar conditions, except that nitric acid rather than hydrochloric acid was used. The precipitate was ignited to the oxide as before. The results obtained were:

Zirconium added, as ZrO_2: 0.1498 ± 0.0002 g.
Zirconium recovered, as ZrO_2: 0.1494 g.
0.1500 g.
0.1501 g.
Average: 0.1498 ± 0.0004 g.

It is clear that thorium and zirconium can be separated in a nitric acid solution as well as in a hydrochloric acid solution.

The mandelic acid was destroyed with potassium permanganate, but when a homogeneous precipitation of the thorium as the 8-quinolinate was attempted, a gelatinous precipitate of undetermined composition was obtained. The precipitate could have been caused by an oxidation product of the mandelic acid, e.g., benzoic acid, benzaldehyde, or benzoyl formic acid.

Because of its lack of promise, this line of investigation was discontinued.

(2) n-Propylarsonic acid: Because of its specificity for zirconium, a separation of thorium and zirconium with n-propylarsonic acid (89) was attempted.

A separation of thorium and zirconium together, from a typical magnesium-base alloy, was carried out with benzoic acid, and the mixed benzoate precipitate was dissolved in hydrochloric acid as described earlier (p.43). Water was added until the solution was 10% with respect to hydrochloric acid and then the solution was heated to boiling. Twenty-five ml. of a hot 5% aqueous solution of n-propylarsonic acid was added to precipitate the zirconium. The precipitate was coagulated, filtered hot on Whatman #40 filter paper, washed with hot water, and finally ignited to the oxide. The results were:

Zirconium added, as ZrO_2: 0.0378 ± 0.0002 g.

Zirconium recovered, as ZrO_2: 0.0373 g.

0.0379 g.

0.0382 g.

Average: 0.0378 ± 0.0005 g.

From these results it is clear that a good separation of thorium and zirconium using n-propylarsonic acid can be effected.

When the filtrate was evaporated and a homogeneous precipitation of the thorium with 8-quinolinol attempted, a white precipitate appeared (probably thorium benzoate).

Further study showed that thorium could not be precipitate with 8-quinolinol in the presence of n-propylarsonic acid. In order for this procedure to be used, a method of destroying the benzoic acid and the n-propylarsonic acid would be necessary. This would make the procedure unnecessarily long and tedious, and so this approach, too, was abandoned.

(3) Dimethyl oxalate: Oxalic acid will precipitate thorium and not zirconium but, if the precipitation is carried out in the classical way, it requires twelve hours. A far more satisfactory method is the homogeneous precipitation of thorium as the oxalate using dimethyloxalate (61).

A solution containing 91.4 mg. of thorium and 37.8 mg. of zirconium was precipitated with benzoic acid as described previously (p.43). The mixed precipitate was dissolved in 25 ml. of hot 7.5 M nitric acid, and 15 M ammonia was added to the point of precipitation of the hydrous oxide. Then 10 ml. of 16 M nitric acid were added, and the solution was allowed to stand for five minutes. Next, six hundred ml. of water and 6 g. of dimethyloxalate were added with stirring. The solution was heated to 85°C. and stirring was continued for thirty minutes. Then 280 ml. of a solution containing 8 g. of oxalic acid were added and the solution stirred for thirty more minutes. The precipitate was filtered and finally ignited. The results were:

Thorium added, as ThO_2:	0.0914 ± 0.0001 g.
Thorium recovered, as ThO_2:	0.0903 g.
	0.0912 g.
	0.0914 g.
Average:	0.0909 ± 0.0006 g.

As can be seen, the use of dimethyloxalate makes possible a reasonably good separation of thorium from zirconium, in the presence of benzoic acid.

Before the thorium could be determined polarographically, the thorium oxalate had to be dissolved, and this could be accomplished conveniently only with potassium permanganate. The use of potassium permanganate introduced manganese(II) ion which is precipitated by 8-quinolinol at about the same pH as thorium is. This complication required another separation, say by the differential precipitation of hydrous oxides. The complications were such as to render unpromising a separational procedure involving dimethyloxalate.

(b) m-Nitrobenzoic Acid

A separation of thorium and zirconium was attempted with m-nitrobenzoic acid.

A solution containing 10.20 mg. of thorium and 15.14 mg. of zirconium was diluted to 50 ml. and the pH adjusted to 0.65 with 7.5 M ammonia, the pH being measured on a pH meter. The zirconium was precipitated by adding 100 ml. of hot 1% aqueous m-nitrobenzoic acid solution of the same pH. The precipitate was coagulated and filtered on Whatman #40 filter paper. The precipitate was then treated as described earlier (p.40) to determine the zirconium content.

The filtrate was allowed to cool and the thorium was precipitated by adjusting the pH to 2.15 with 7.5 M ammonia, measuring the pH on a pH meter. The precipitate was coagulated by heating near the boiling point for fifteen minutes, and was filtered on Whatman #40 filter paper. The thorium m-nitrobenzoate precipitate was then treated as described earlier (p.21) to determine the thorium content.

Zirconium added:	15.14 ± 0.01 mg.
(by gravimetric determination as ZrO_2)	
Zirconium recovered:	15.14 ± 0.03 mg.
	15.14 ± 0.07 mg.
	15.18 ± 0.04 mg.
Average:	15.15 ± 0.03 mg.
Thorium added:	
(by gravimetric determination as ThO_2)	10.20 ± 0.01 mg.
Thorium recovered:	10.19 ± 0.08 mg.
	10.27 ± 0.06 mg.
	10.24 ± 0.03 mg.
Average:	10.23 ± 0.04 mg.

As can be seen from these results, a separation of thorium and zirconium is possible using m-nitrobenzoic acid and pH control.

(ii) By Ion Exchange

It was found that the separation of thorium from zirconium, and from other elements that precipitate with m-nitrobenzoic acid, can be conveniently and efficiently carried out by means of an ion exchange column, as shown by the experiments described below. For reasons given earlier, an anion rather than cation exchange resin was used; in all these experiments the resin was Dowex 1.

After the columns had been prepared and "conditioned" as described earlier (p.12), they were rinsed with 30 ml. of hydrochloric acid of the same molarity as was used in the separation to follow. The level of the acid in the column was lowered until the meniscus barely touched the wad of glass wood on top of the resin. A 5.00 ml. aliquot sample of the solution containing the ion to be separated was then pipetted onto the column and the column was then drained until the meniscus again touched the wad of glass wool. The resin was then washed with hydrochloric acid of the same concentration by passing 5 ml. portions of it through the column until the non-exchanging ions had been washed out of the column.

When ions were to be eluted from a column, hydrochloric acid of an appropriate concentration was passed through the column in 5 ml. portions as described above.

(a) The Separation of Thorium and Zirconium

<u>(1) Sorption and elution of zirconium</u>: The sorption of zirconium from hydrochloric acid solutions was studied colorimetrically using alizarin red S (90). The zirconium content was measured in order to determine how efficient the column was in sorbing the zirconium from solutions of hydrochloric acid of various concentrations.

Solutions of constant zirconium content but of varying hydrochloric acid concentration were prepared from recrystallized zirconium oxychloride. The columns were rinsed with 30 ml. of the concentration of hydrochloric acid to be used in the sorption and a 5.00 ml. aliquot sample of the zirconium solution, containing about 10 mg. of zirconium, was pipetted onto the column. The solution was allowed to drain into the resin, and then the resin was washed with hydrochloric acid of the same concentration, using 5 ml. at a time. Each 5 ml. of the washings was analyzed colorimetrically for zirconium, using the procedure of Wengert (60), and the results for the sorption from 8, 9, 10, and 11 M hydrochloric acid are given below.

As is readily seen from Figure XIV, zirconium is not sorbed to any appreciable extent from 8 M hydrochloric acid. From 9 M hydrochloric acid the zirconium is sorbed, but, after 30 ml. of washing, some zirconium begins to appear in the washings. From 10 M and 11 M hydrochloric acid zirconium is strongly sorbed by the resin, since none appeared in the washings even after 50 ml. of washing.

The elution of zirconium from the resin was studied by passing 4 M hydrochloric acid through a column containing the sorbed zirconium and determining, colorimetrically with alizarin red S (90), the amount of zirconium in each 5 ml. of washing liquid drained from the column. The results are shown in Figure XV. As can be seen from this graph, after 40 ml. of 4 M hydrochloric acid had been passed through the column, no zirconium could be detected in the elutriant. In order to ensure complete removal of the zirconium, 60 ml. of elutriant were used in all subsequent analyses.

To determine if the elution of the zirconium with 4 M hydrochloric acid was quantitative, 33 mg. of zirconium in 5 ml. of 10 M hydrochloric acid was placed on the column as before and the resin washed with 60 ml. of 10 M hydrochloric acid. Sixty ml. of 4 M hydrochloric acid were then passed through the column and caught in a 250 ml. volumetric flask. Aliquot samples of this solution were analyzed for zirconium colorimetrically

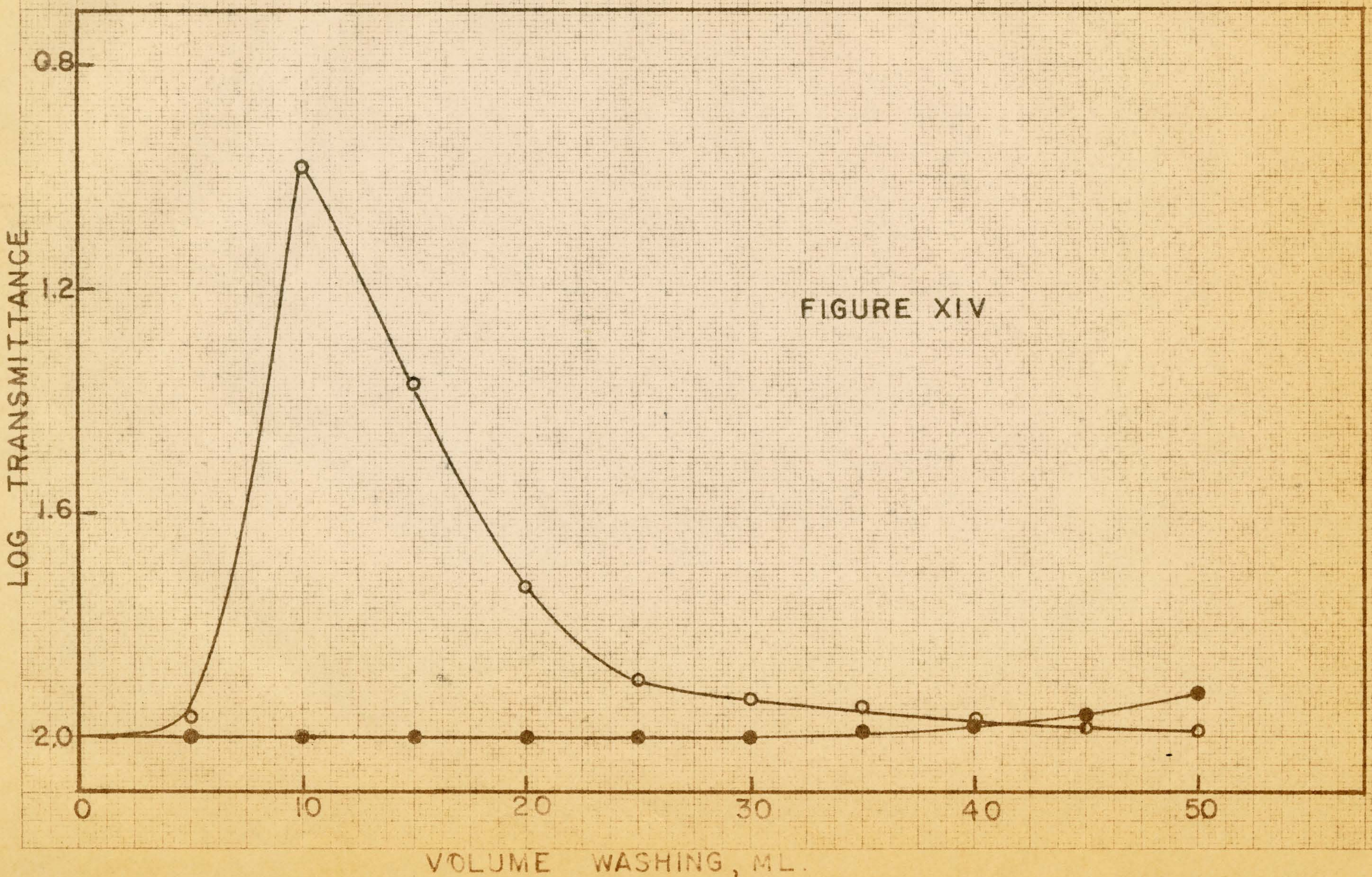

LOG TRANSMITTANCE
0.8
1.2
1.6
2.0
0
10
20
30
40
50
VOLUME WASHING, ML.

FIGURE XIV

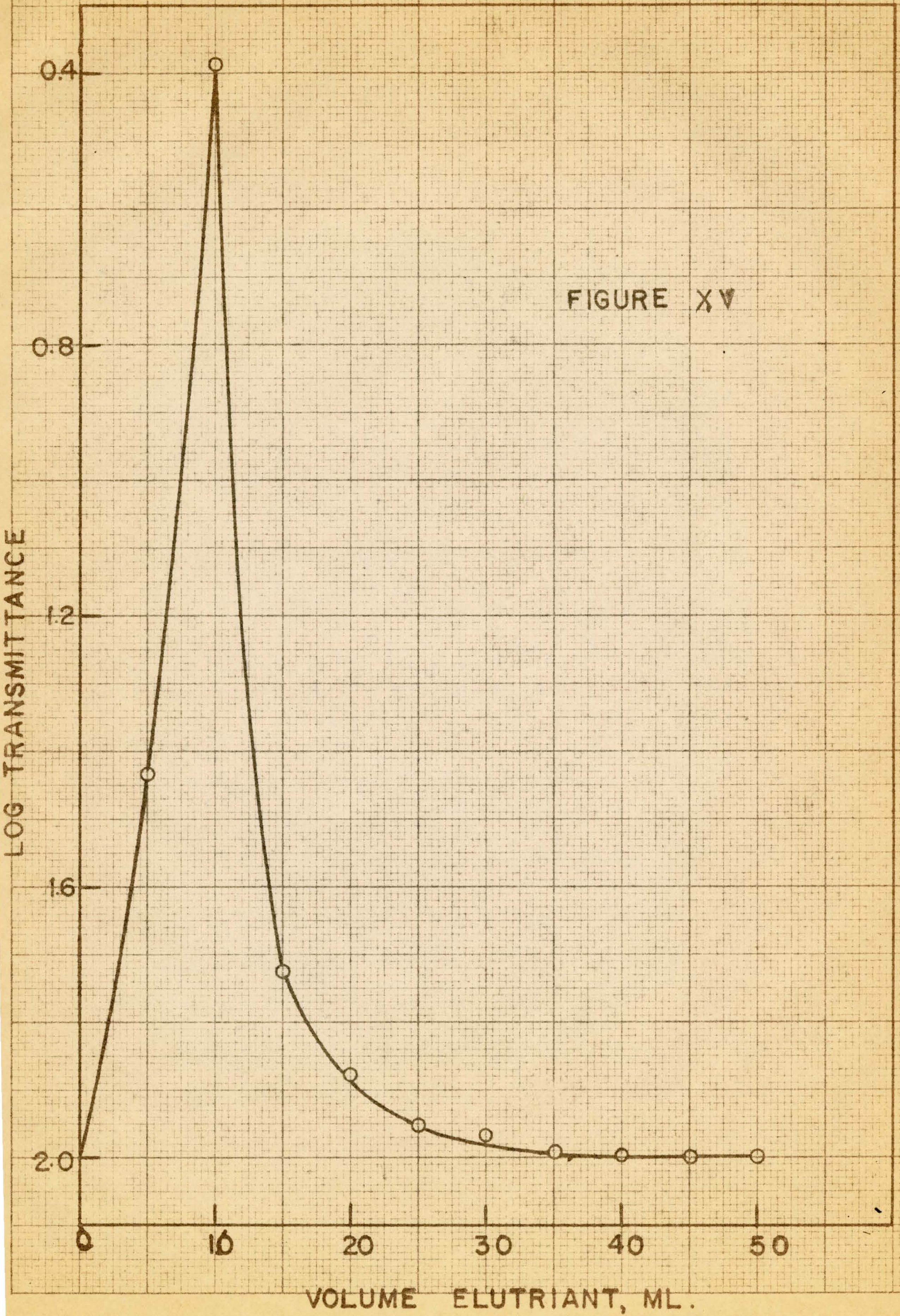

0.4
0.8
1.2
1.6
2.0
LOG TRANSMITTANCE
0
10
20
30
40
50
VOLUME ELUTRIANT, ML.

FIGURE XV

with alizarin red S. At the same time, an identical zirconium solution that had not been passed through the column was analyzed in a similar manner. The results were:

	Transmittance
Standard zirconium solution:	62.0 ± 0.2%
	62.9 ± 0.3%
Zirconium solution eluted from the column:	61.8 ± 0.3%
	62.6 ± 0.4%

From these results it is apparent that zirconium can be quantitatively sorbed on Dowex 1 resin from 10 M hydrochloric acid, and quantitatively eluted from the resin with 4 M hydrochloric acid.

(2) Quantitative recovery of thorium: An investigation of the sorption of thorium on Dowex 1 resin from 12 M hydrochloric acid was carried out. Determinations of thorium in the washings were made colorimetrically using 1-(o-arsonophenylazo)-2-naphthol-3:6-disulphonic acid (9).

A 5.00 ml. aliquot sample of a 12 M hydrochloric acid solution containing 9.73 mg. of thorium was pipetted onto the column. The solution was allowed to drain into the resin, and then the column was washed with 60 ml. of 12 M hydrochloric acid, using 5 ml. portions. Each 5 ml. of washings was caught in a 100 ml. volumetric flask and tested colorimetrically for thorium. The results are shown in Figure XVI. From this figure, it is apparent that no significant amounts of thorium were removed from the column after 45 ml. of acid had come through the column. In order to be certain of complete removal of thorium, the columns were washed with 60 ml. of wash solution in all subsequent experiments.

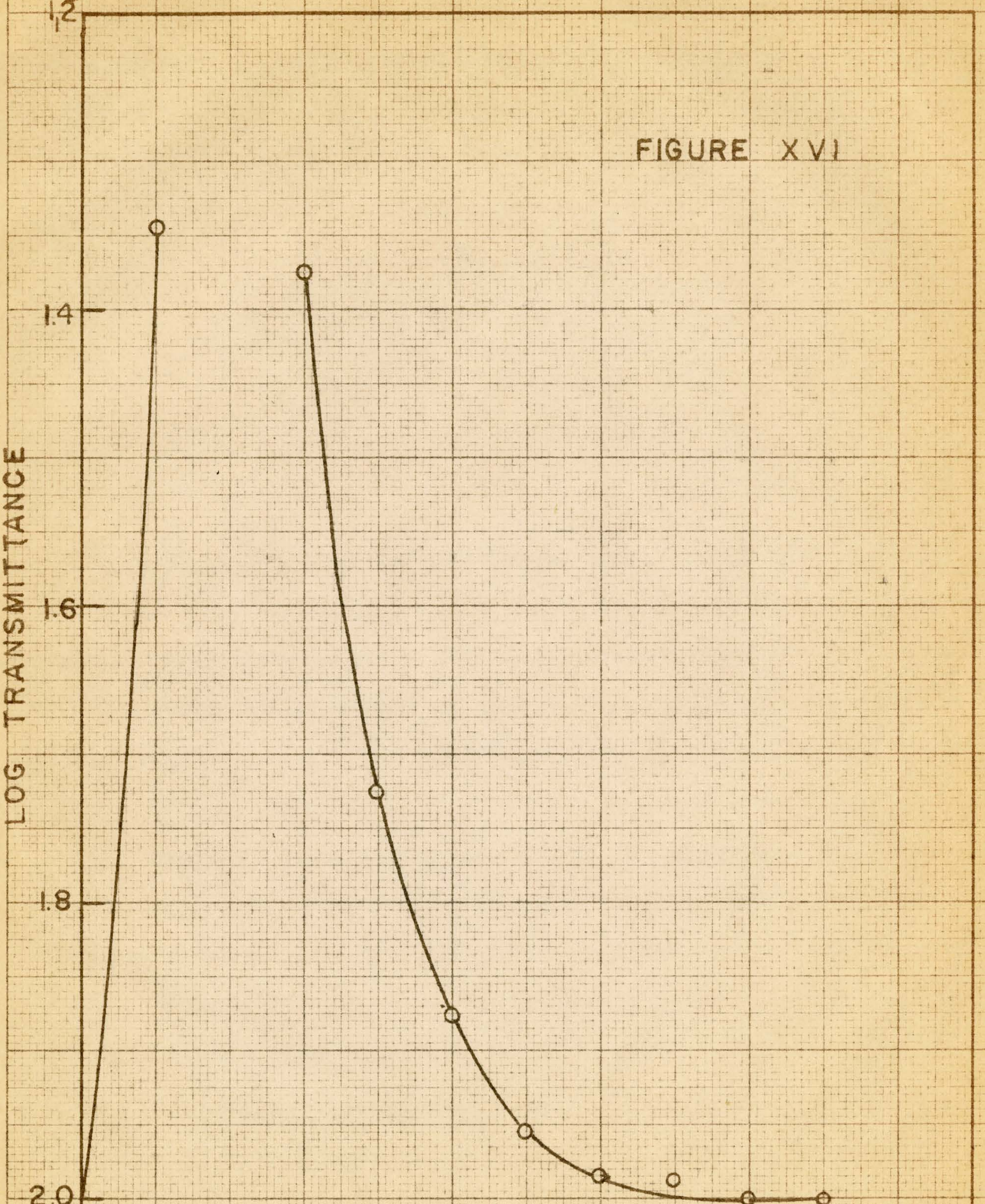


FIGURE XVI
LOG TRANSMITTANCE
1.2
1.4
1.6
1.8
2.0
0
10
20
30
40
50
VOLUME WASHING, ML.

A similar experiment was carried out in which the washings were collected and the thorium content determined polarographically by precipitation with m-nitrobenzoic acid, according to the method described earlier (p.21). The results were as follows:

Thorium put through the column: (by gravimetric determination)	8.80 ± 0.01 mg.
Thorium recovered in 60 ml. of washings:	8.78 ± 0.07 mg.
	8.82 ± 0.06 mg.
	8.76 ± 0.07 mg.
Average:	8.79 ± 0.03 mg.

It is evident from these results that thorium in 12 M hydrochloric acid, at least in the amounts used in these experiments, can be quantitatively washed from the column with 60 ml. of wash solution.

A separation of thorium and zirconium in 10 M hydrochloric acid was attempted. The column was rinsed with 30 ml. of 10 M hydrochloric acid and a 5.00 ml. aliquot sample containing 8.80 mg. of thorium and 33 mg. of zirconium was pipetted onto the column. The aliquot sample was allowed to drain through the column and then the column was washed with 60 ml. of 10 M hydrochloric acid. All washings were collected and analyzed polarographically for thorium with m-nitrobenzoic acid as described above (p.21). The results were as follows:

Thorium added to the column: (by gravimetric determination)	8.80 ± 0.01 mg.
Thorium recovered:	8.77 ± 0.07 mg.
	8.79 ± 0.02 mg.

From these data it can be seen that a separation of thorium and zirconium on Dowex 1 resin from 10 M hydrochloric acid is possible.

(b) The Separation of Thorium from Other Elements

According to Osborn (64), titanium and cerium(IV) are precipitated by m-nitrobenzoic acid, and tin and mercury interfere on account of hydrolysis effects. The interference of cerium can be overcome by reducing it to cerium(III).

(1) Mercury: An attempt was made to separate thorium and mercury(II) under the conditions developed for the thorium-zirconium separation, without a preliminary study of the sorption of mercury(II) on Dowex 1 resin from hydrochloric acid solutions.

A 5.00 ml. aliquot sample containing 9.73 mg. of thorium and 45 mg. of mercury(II) in 10 M hydrochloric acid was placed on the column after rinsing the column as before. The column was washed with 60 ml. of 10 M hydrochloric acid and the thorium content of the washings was determined polarographically using m-nitrobenzoic acid as described earlier (p .21). The results were as follows:

Thorium added to the column: 9.73 ± 0.01 mg.
(by gravimetric analysis)
Thorium recovered: 9.72 ± 0.09 mg.
9.76 ± 0.06 mg.

From these results it is apparent that thorium can be determined without interference from mercury(II) under the conditions used for the separation of thorium and zirconium.

(2) Titanium: An investigation of the sorption of titanium on

Dowex 1 resin from hydrochloric acid solutions was carried out by analyzing the washings from the column colorimetrically with hydrogen peroxide (91).

Five ml. aliquot samples containing 30 mg. of titanium in 10, 11 and 12 M hydrochloric acid were pipetted onto three columns, from stock solutions of titanium tetrachloride. The columns were washed with a corresponding concentration of hydrochloric acid, 5 ml. at a time, and each 5 ml. of washing were analyzed colorimetrically for titanium. It was found that titanium was not sorbed to any appreciable extent from 10, 11, or 12 M hydrochloric acid.

The hydrogen chloride content of the solution of titanium chloride was increased beyond 12 M by bubbling gaseous hydrogen chloride through the solution at room temperature for twenty minutes. A 5.00 ml. aliquot sample of this solution was put on the column and washed through the resin with a hydrochloric acid solution that had been treated in the same way. The titanium was only weakly sorbed, for after 25 ml. of washing the wash solution gave a pronounced test for titanium.

Finally, gaseous hydrogen chloride was bubbled through a solution of titanium tetrachloride in 12 M hydrochloric acid which was kept cool in an ice-water mixture. After fifteen minutes of bubbling, the solution was allowed to warm to room temperature with frequent agitation to avoid supersaturation. A 5.00 ml. aliquot sample of this solution was pipetted onto the column and the column was washed with hydrochloric acid prepared in the same way. The washings from the column, when tested as before, gave a negative test for titanium even after 75 ml.of washing.

A separation of thorium and titanium was attempted using a solution saturated with hydrogen chloride as described above. A 5.00 ml. aliquot sample containing 9.73 mg. of thorium and 30 mg. of titanium was placed in the column, under the conditions described above, and washed through the column with 60 ml. of the aforementioned wash solution. The washings were collected and analyzed polarographically with m-nitrobenzoic acid as described earlier (p.21). The results are as follows:

Thorium added to the column: (by gravimetric analysis)	9.73 ± 0.01 mg.
Thorium recovered in washings:	9.74 ± 0.05 mg. 9.75 ± 0.07 mg.

From these results it can be seen that a separation of thorium and titanium is possible when they are present in very concentrated hydrochloric acid.

(3) Tin: The sorption of tin(II) from hydrochloric acid solutions on Dowex 1 resin was studied by analyzing the washings from the column colorimetrically for tin(II) with cacotheline (92).

Five ml. aliquot samples of tin(II) chloride solutions containing 30 mg. of tin in 8, 9, 10, 11 and 12 M hydrochloric acid were pipetted onto the column. The column was washed with hydrochloric acid of the same concentration, and each 5 ml. of washings were tested for tin(II) by means of cacotheline. From 11 and 12 M hydrochloric acid, the washings gave a positive test for tin(II) and after 15 ml. of washing; from 10 M, a positive test was obtained after 35 ml. of washing; and from 9 M, a positive test after 40 ml. of washings. From 8 M hydrochloric acid the tin(II) was still retained on the column after 60 ml. of washing.

A separation of thorium and tin(II) in 8 M hydrochloric acid was attempted by placing on the column a 5.00 ml. aliquot sample containing 9.75 mg.

of thorium and 30 mg. of tin(II). The column was washed with 60 ml. of 8 M hydrochloric acid; the washings were collected and analyzed polarographically for thorium with m-nitrobenzoic acid as described earlier (p.21). The results were as follows:

Thorium added to the column: 9.73 ± 0.01 mg.
(by gravimetric determination)
Thorium recovered in the washings: 9.74 ± 0.07 mg.
9.76 ± 0.04 mg.

From these results it is apparent that a separation of thorium and tin on Dowex 1 resin from 8 M hydrochloric acid is possible.

In Table I there are summarized the conditions used for the ion exchange separations of thorium from other elements.

Table I

SEPARATIONS OF THORIUM FROM MERCURY, TIN, AND TITANIUM

	Tin(II)	Mercury(I)	Titanium(IV)
mg. of element in 5.00 ml. of solution	30	45	30
concentration of hydrochloric acid: in solvent (5.00 ml.)	8 M	10 M	12 M saturated with hydrogen chloride
in wash solution (60 ml.)	8 M	10 M	12 M saturated with hydrogen chloride
mg. of thorium present in 5.00 ml. portion	9.73	9.73	9.73
mg. of thorium recovered after column separation	9.75	9.74	9.75

(D) Procedure for Analysis of Alloys

(i) Zirconium-free Magnesium-base Alloys

(a) Procedure

To an accurately weighed 2.5 g. sample of alloy, about 25 ml. of water are added, followed by sufficient 12 M hydrochloric acid (about 25 ml.) in small amounts to cause complete dissolution of the sample without applying heat. The solution is transferred to a 250 ml. volumetric flask along with 25 ml. of 12 M hydrochloric acid and made up to the mark with water.

To a 25 ml. aliquot sample of this solution there are added 50 ml. of saturated m-nitrobenzoic acid solution. The thorium m-nitrobenzoate is precipitated by adjusting the pH of the solution to 2.15 ± 0.10 using 7.5 M ammonia (about 3 ml. are required); the pH is measured by means of a pH meter. The precipitate is coagulated by heating the mixture near the boiling point for about fifteen minutes, and then is filtered on Whatman #40 filter paper. The precipitate is carefully washed with hot water and dissolved directly into a 100 ml. volumetric flask by means of hot perchloric acid (one volume 72% perchloric acid to two volumes of water). Five ml. of 20% tartaric acid solution are then added and the solution is adjusted to the methyl red end point using 15 M ammonia. Thirty-five ml. of saturated potassium hydrogen phthalate solution and ten drops of a 1% solution of α-naphthol in ethyl alcohol are added, and the solution made up to the mark with water. A portion of the solution is decanted into a polarographic cell, bubbled with purified nitrogen for ten minutes, and then polarographed.

The average height of five waves for the reduction step of m-nitrobenzoic acid is taken and the corresponding concentration of thorium is assessed by reference to a calibration curve (Figure III). The calibration curve is prepared in a similar manner, with solutions of known thorium content. The calibration solutions were prepared by dissolving purified thorium tetrachloride in 5% hydrochloric acid, and the thorium content was determined by precipitation of the hydrous oxide using ammonia, followed by ignition to thorium dioxide.

(b) Testing of the Procedure

The procedure that was developed for the determination of thorium in zirconium-free magnesium-base alloys was tested by analyzing solutions of known thorium content that contained magnesium, zinc, rare earth elements and other elements that are present in such alloys. The composition of the synthetic alloy solutions corresponded to that of commercial alloys or to that of alloys of more complex composition.

The synthetic alloy solutions were prepared from stock solutions of thorium, magnesium, zinc and rare earth elements as the chlorides, so that the solutions would correspond to those obtained by dissolving a sample of the alloy in hydrochloric acid as required by the procedure. The concentrations were chosen so that after mixing and diluting, a 25 ml. aliquot sample (that taken for analysis) would have the composition shown in Table II.

The synthetic alloy solutions were analyzed by the method as outlined under the procedure for thorium in magnesium-base alloys. The results of these analyses are shown in Tables III and IV.

Table II

SOURCE OF IONS FOR AND COMPOSITION OF SYNTHETIC ALLOY SOLUTIONS

Element	Source of Ion	Approximate Composition, %
Magnesium	Metal	69 - 85
Zinc	Metal	5.7 - 7.0
Iron	Impurities in Zinc and Mischmetal	0.21 - 0.26
Cerium	Mischmetal	10 - 1.7
Other Rare Earth Elements	Mischmetal and Lanthanum Nitrate	12 - 2.3
Thorium	Purified $ThCl_4$	3.1 - 3.8
Manganese	$MnCl_2$	Approx. 0.01
Lead	$PbCl_2$	Approx. 0.01
Aluminium	Metal	Approx. 0.01
Copper	Metal	Approx. 0.01

Table III

ANALYSES OF SYNTHETIC ALLOY SOLUTIONS

(All solutions contained 230 mg. of magnesium, 19 mg. of zinc, 0.7 mg. of iron and traces of aluminium, manganese, lead and copper)

Rare Earth Elements Present, %	Thorium Added, %	Thorium Found, %
4.0	3.76	3.77 ± 0.03
7.8	3.62	3.63 ± 0.03
15.8	3.30	3.31 ± 0.03
21.9	3.06	3.06 ± 0.01
21.9	3.06	3.04 ± 0.03

Table IV

ANALYSES OF SYNTHETIC ALLOY SOLUTIONS

(All solutions contained 230 mg. of magnesium, 19 mg. of zinc, 0.7 mg. of iron and traces of aluminium, manganese, lead and copper)

Rare Earth Elements Present, %	Thorium Added, %	Thorium Found, %
As Mischmetal		
4.1	2.29	2.27 ± 0.03
7.9	2.20	2.21 ± 0.03
As $La(NO_3)_3$		
4.6	2.28	2.27 ± 0.03
2.4	2.34	2.33 ± 0.02

(ii) Zirconium-containing Magnesium-base Alloys

(a) Procedure

To a 5-g. sample of the alloy is added carefully, and in small amounts, 12 M hydrochloric acid (about 70 ml.) until dissolution of the alloy is complete. (To hasten the dissolution, the solution may be heated after the initial reaction has subsided.) The solution is transferred to a 100 ml. volumetric flask with 12 M hydrochloric acid and diluted to the mark with 12 M hydrochloric acid.

After thoroughly rinsing a Dowex 1 ion exchange column with 10 M hydrochloric acid as described previously (p. 12), a 5.00-ml. aliquot sample of the alloy is placed on the column and allowed to drain to the top of the resin. The column is then washed with 60 ml. of 10 M hydrochloric acid, and the washings are caught in a 250 ml. beaker. Fifty ml. of saturated m-nitrobenzoic acid solution and 37 ml. of 15 M ammonia are added. The solution is allowed to cool to room temperature. Then the thorium m-nitrobenzoate is precipitated by adjusting the pH to 2.15 ± 0.10 with 7.5 M ammonia, measuring the pH on a pH meter. The procedure from this point on is identical with that given earlier (p.60) for the determination of thorium in zirconium-free magnesium-base alloys.

(b) Testing the Procedure

The procedure that was developed for the determination of thorium in zirconium-containing magnesium-base alloys was tested by analyzing solutions of known thorium content that contained magnesium, zinc, rare earths and other elements in concentrations that correspond to the composition of such alloys or to those of more complex alloys.

The synthetic alloy solutions were prepared from stock solutions of magnesium, zinc, thorium, zirconium and the rare earth elements as the chlorides in 10 M hydrochloric acid. Variously sized aliquot samples of the stock solution were taken so that, after mixing and diluting to volume, a sample of the solution would contain the elements in proportions corresponding to the alloy compositions shown in Table V.

The alloys were analyzed by the method as outlined under the procedure for thorium in zirconium-base alloys. The results of these analyses are shown in Table VI.

Table V

ALLOY COMPOSITIONS CORRESPONDING TO SYNTHETIC SOLUTIONS

Metal	Composition of Alloy, %
Magnesium	74 - 82
Zinc	6.2 - 6.8
Iron	0.23 - 0.25
Cerium	6.7 - 3.6
Other Rare Earth Elements	7.7 - 4.2
Thorium	3.1 - 3.4
Zirconium	1.9 - 1.0
Aluminium	Approx. 0.01
Lead	Approx. 0.01
Copper	Approx. 0.01
Manganese	Approx. 0.01

Table VI

ANALYSES OF SYNTHETIC MAGNESIUM-BASE ALLOY SOLUTIONS

(All solutions contained 230 mg. of magnesium, 19 mg. of zinc, 0.7 mg. of iron and traces of aluminium, manganese, lead and copper)

Zirconium Present, %	Rare Earth Elements Present, %	Thorium Added, %	Thorium Found, %
0	7.8	3.39	3.39 ± 0.01
1.0	7.7	3.35	3.35 ± 0.02
1.0	7.7	3.35	3.33 ± 0.01
2.0	7.6	3.32	3.32 ± 0.02
2.0	7.6	3.32	3.30 ± 0.01
1.8	14.2	3.08	3.07 ± 0.02
1.8	14.2	3.08	3.06 ± 0.02

(E) Composition of Precipitates

(i) Thorium

The composition of thorium m-nitrobenzoate was determined by precipitating, by the method described on page 21, a known amount of thorium, dissolving the precipitate in acid, and determining the amount of m-nitrobenzoic acid polarographically. The calibration curve was prepared by polarographing aliquot samples of a standard m-nitrobenzoic acid solution. This solution was prepared by dissolving a carefully weighed quantity of thrice recrystallized m-nitrobenzoic acid in hot water, transferring the solution to a 1000 ml. volumetric flask, and diluting the solution to volume at 25°C. with water. To each aliquot sample, in a 100 ml. volumetric flask, was added perchloric acid in an amount equal to that used in the dissolution of the precipitate. The solution was adjusted to the methyl red end point with 15 M ammonia. Thirty-five ml. of saturated potassium hydrogen phthalate solution and 10 drops of a 1% solution of α-naphthol in ethyl alcohol were added and the solution was diluted to the mark with water. A portion of the solution was decanted into a polarographic cell, bubbled with purified nitrogen for ten minutes, and polarographed. Good calibration curves were obtained using this procedure.

Various amounts of thorium were precipitated, and the ratios of thorium to m-nitrobenzoic acid that were found are shown in Table VII.

Table VII

COMPOSITION OF THORIUM m-NITROBENZOATE

Thorium taken moles x 10^4	m-Nitrobenzoic acid found, moles x 10^4	Number of moles of m-nitrobenzoic acid to one mole of thorium
0.803	3.19	3.97
1.605	6.4_6	4.03
2.410	9.5_9	3.98
3.211	12.6_5	3.94
4.015	15.9_1	3.96
	Average:	3.98 ± 0.05
4.81	19.2	3.98
4.81	19.1	3.96
4.81	19.0	3.95
	Average:	3.96 ± 0.02

(ii) Zirconium

The composition of zirconium m-nitrobenzoate was determined in a manner similar to that used for thorium m-nitrobenzoate. Various amounts of zirconium were precipitated, and the ratios of zirconium to m-nitrobenzoic acid found are shown in Table VIII.

Table VIII

COMPOSITION OF ZIRCONIUM m-NITROBENZOATE

Zirconium taken, moles x 10^5	m-Nitrobenzoic acid found, moles x 10^5	Number of moles of m-nitrobenzoic acid to one mole of zirconium
1.66	2.8	1.69
3.32	5.6	1.68
6.64	10.5	1.58
8.30	12.9	1.56
9.96	15.5	1.56
13.29	20.7	1.56
13.29	20.7	1.56
13.29	20.9	1.58

DISCUSSION

This work has shown that thorium can be determined by polarographic methods using one or other of the reagents 8-quinolinol, m-nitrobenzoic acid or m-nitrophenylarsonic acid, as both a precipitating agent and a polarographically reducible substance. The methods involve the quantitative precipitation of thorium, under controlled conditions, by the organic reagent, then the dissolution of the filtered and washed precipitate, and finally the polarographic determination of the free organic reagent that results from the dissolution. By appropriate calibration procedures, the amount of the organic reagent found can be related to the amount of thorium in the original solution. A more indirect method, involving the addition of a carefully measured amount of the organic reagent to the thorium solution, and the determination of the excess of organic reagent after precipitation of the thorium, is also likely feasible using any one of the organic reagents mentioned. The validity of this approach has been demonstrated, however, only in the case of 8-quinolinol.

The conditions under which thorium gives, with each of these organic reagents, a precipitate that is analytically useful have been found to be not unduly restrictive. The precipitates are readily soluble in appropriate media under conditions that are conveniently achieved, and each of the organic reagents gives an easily measured polarographic wave. In each instance a strictly linear relationship between the diffusion current of the reagent and its concentration has been demonstrated.

8-Quninolinol has long been used for the gravimetric determination of thorium, but in this work an improved method for the precipitation has resulted from the adoption of a homogeneous precipitation procedure.

The thorium 8-quinolinate obtained by this procedure is readily filtered and washed, in contrast to the precipitate obtained by the commonly used procedure of Frere (86), which suggests the use of a glass frit and suction. The homogeneous method also ensures that the thorium 8-quinolinate precipitate has the composition $Th(C_9H_6ON)_4 \cdot C_9H_6OHN$. The extra mole of 8-quinolinol is obtained only when the precipitation is carried out above 70°C. (86), as it is in the homogeneous method. At temperatures below 70°C., a mixed precipitate of $Th(C_9H_6ON)_4$ and $Th(C_9H_6ON)_4 \cdot C_9H_6OHN$ is obtained (86). Such a mixed precipitate is not objectionable in gravimetric analysis where the precipitate is ignited to thorium dioxide, but it is not analytically useful for polarographic work, since there would not be a linear relationship between the concentration of thorium and the diffusion current given by the 8-quinolinol after dissolution of the precipitate.

Although the two polarographic procedures that were developed for the determination of thorium using 8-quinolinol are very convenient, they have the pronounced disadvantage of being restricted in application owing to the lack of specificity of 8-quinolinol. This property of 8-quinolinol makes it an unattractive reagent on which to base a method for the determination of thorium, or almost any element, when a substantial number of other elements may be present. Although good separations of elements using 8-quinolinol have been reported (25, 29), the homogeneous procedure for thorium that has been developed in this work would need further development before close and reliable control of pH could be achieved. Such a control of pH could very likely be obtained by carefully adjusting the pH of the solution and then adding a carefully weighed amount of urea.

The precipitation of thorium by m-nitrophenylarsonic acid, although restricted to a pH range of 1.4 to 2.6, is more attractive than the 8-quinolinol procedure because of the greater specificity of m-nitrophenylarsonic acid. According to Kolthoff and Johnston (57), m-nitrophenylarsonic acid precipitates iron(III) as well as tin(IV) and other quadrivalent metals. The procedure involving m-nitrophenylarsonic acid that was developed in this work is, however, rather lengthy because a two-hour standing period is required in order to ensure complete precipitation of thorium m-nitrophenylarsonate. The use of heat to hasten the coagulation of the precipitate was deemed unwise in view of the work of VanDalen (97) on the determination of titanium with m-nitrophenylarsonic acid.

The method for thorium using m-nitrobenzoic acid combines the speed of the 8-quinolinol procedure and the specificity of the m-nitrophenylarsonic acid procedure. The range of allowable pH values for precipitation, though narrow, is practical. The range of pH values that has been found appropriate differs from that recommended by Osborn (64), but this may in part be due to differences in procedures: amount of reagent, use of a chloride system rather than a nitrate system, etc.

It has been shown by a polarographic method that, under the conditions of precipitation used, the precipitate has the composition $Th(C_6H_4NO_2COO)_4$. This is in agreement with the results of other workers who used different methods of analysis (81, 94).

Attention was also given in this work to a polarographic method for the determination of zirconium, using m-nitrobenzoic acid. Although the procedure that was developed differs little from that proposed by Graham et. al. (59), the conditions for the precipitation have been more firmly established. The importance of a large excess of reagent has been demonstrated and it has been shown that the concentration of zirconium, precipitated by a constant amount of m-nitrobenzoic acid, affects the composition of the precipitate. Over a reasonably broad pH range a precipitate of constant composition containing 1.56 moles of m-nitrobenzoic acid for every mole of zirconium was obtained.

The present work has also been concerned with separating thorium, and to lesser extent zirconium, from substances that interfere with their determination, particularly the interfering substances likely to be present in modern magnesium-base alloys. The most serious problem is the separation of thorium and zirconium.

The separation of thorium and zirconium by precipitation methods has in general been shown in this work not to be attractive, particularly when the thorium is to be subsequently determined polarographically. Although effective separations could be achieved, they were usually tedious, and yielded solutions containing substances that were undesirable.

A separation using mandelic acid as a precipitant for zirconium, although it was shown to be quantitative in both nitric acid and hydrochloric acid media, is not useful since the thorium is apparently strongly complexed by the excess mandelic acid. Procedures using dimethyl oxalate and n-propylarsonic acid, although also successful as separations, were discarded owing to the difficulty of destroying the residual organic reagents before the precipitation of thorium.

The separation of thorium and zirconium by means of m-nitrobenzoic acid is much more encouraging. A separation, and subsequent determination, of thorium and zirconium with m-nitrobenzoic acid using pH control was carried out with good results. Osborn (64) has reported a similar separation but Venkataramaniah, et. al. (65) were unable to duplicate his results. This failure could have been due to lack of the close control of pH necessary for the quantitative precipitation of thorium, or failure to use a large excess of reagent in the precipitation of zirconium, or both. The separation of thorium and zirconium by means of m-nitrobenzoic acid was not exploited because, by the time it was shown to be promising, an attractive ion-exchange method had claimed more interest.

The separation of thorium from zirconium can be very simply and very effectively carried out by means of an anion exchange column. The separation depends on the formation of an anionic chlorido complex ion of zirconium in concentrated hydrochloric acid. If these elements in 10 M hydrochloric acid solution are passed through a Dowex 1 column, the zirconium is quantitatively retained, and the thorium can be quantitatively washed from the column with 10 M hydrochloric acid. This separation introduces no substances that cause interference in the polarographic methods for thorium that have been discussed earlier. If a determination of zirconium is desired, this element can be quantitatively eluted from the column by means of 4 M hydrochloric acid. (Water is unsatisfactory as an eluting agent because of the ease with which zirconium hydrolyzes.)

The anion exchange method for the separation of zirconium and thorium, and the polarographic method for thorium using m-nitrobenzoic acid, have been applied to synthetic solutions. One group of solutions contained magnesium, zinc, rare earth elements, zirconium and other elements, in proportions that corresponded to those that are obtained by dissolving modern magnesium-base alloys, or more complex alloys. The results were very satisfactory, both as regards precision and accuracy, and demonstrated the validity of the separational and polarographic procedures that have been developed. If zirconium is not present, as is true of some thorium-magnesium alloys, the ion-exchange procedure is unnecessary. Under these circumstances, the polarographic procedure can be applied directly to a solution of the alloy, as experiments with another group of synthetic alloy solutions demonstrated.

Titanium, mercury and tin are elements that, although not present in thorium-magnesium alloys, furnish ions that can interfere with the precipitation of thorium by m-nitrobenzoic acid. In order to broaden the range of application of the polarographic method for thorium, using m-nitrobenzoic acid, some study was given to ion-exchange methods for separating thorium from each of titanium(IV), mercury(II) and tin(II).

The ion-exchange separation of thorium and titanium using Dowex 1 can be effected in hydrochloric acid solution saturated with hydrogen chloride. Owing to the very large excess of hydrogen chloride in the solution, gassing that can block the column may occur. This can usually be overcome by taking care to avoid supersaturating the solution with hydrogen chloride. As shown earlier, the determination of thorium in the presence of titanium by this method gives good results.

A determination of thorium in a solution that initially contained mercury(II) was carried out with good results. A procedure that is identical to that used for the thorium-zirconium separation was found to be applicable to mercury(II), and therefore little study was given to the exact conditions for the sorption of mercury(II) from hydrochloric acid solutions.

It was also found that an efficient separation of thorium from tin(II) can be carried out in 8 M hydrochloric acid. The elution of the tin(II) from the column is not as easily effected as that of the other elements studied. Large volumes (ca. 300-500 ml.) of elutriant (water or 0.1 M HCl) were necessary for the complete removal of tin(II). Kraus (96) had found the same phenomenon with Pt(IV) and Pd(II) and states it to be characteristic of elements from which the concentration of the sorbable species does not increase with increasing concentration of hydrochloric acid.

These experiments, together with those involving thorium and zirconium, have shown that ion-exchange procedures lend themselves well to removing elements that interfere with the precipitation of thorium by means of m-nitrobenzoic acid. This method, then, is applicable to the determination of thorium in more substances than the magnesium-base alloys for which it was specifically developed.

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APPENDIX

Purification of Reagents

(a) Dimethyl Oxalate

Slurry the freshly recrystallized dimethyl oxalate, prepared by the method of Bowden (76), with methanol that has been cooled to -40°C. with Dry Ice, and quickly filter. Repeat this procedure until a negative test for sulphate is obtained.

(b) Thorium Tetrachloride

Prepare a hot saturated solution of the commercial salt and cool to room temperature. Saturate the solution with hydrogen chloride and add an equal volume of ethyl ether. Stir until crystallization is complete, then filter and wash several times with ether. Dry the purified salt at room temperature *in vacuo*.

(c) Zirconium Oxychloride

Prepare a cold saturated solution of the commercial salt, and add an equal volume of 12 M hydrochloric acid. Stir until crystallization is complete; then filter and wash several times with cold 12 M hydrochloric acid. Dry the purified salt at room temperature *in vacuo*.