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PRELIMINARY REPORT ON METHODS OF ANALYSIS FOR VERY SMALL PERCENTAGES OF THORIUM

PART I

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ABSTRACT

Detailed procedures are presented for the determination of very small percentages of thorium. The methods are designed to determine 0.001% of thorium oxide as the lower limit and are applicable to silicate and phosphate rocks. For quantities below a milligram of ThO_2, the thorium is determined nephelometrically as the iodate or photometrically with p-dimethylaminoazophenylarsonic acid. For quantities of thorium above one milligram of ThO_2, the thorium is determined gravimetrically. A discussion of the important features of the methods and a summary of the more important experimental work that lead to the adoption of the procedures is given.

INTRODUCTION

In the work of the Trace Elements Project of the Geological Survey, it was necessary to know the thorium content of samples for which measurements of total radioactivity and uranium content had been made. Methods had to be developed by which accurate determinations of very small percentages of thorium could be made on rocks and ores of widely varying types. This report presents some of the procedures developed in the Chemical Laboratory of the Geological Survey and now in use, and is preliminary. Further work is in progress on these and other methods, including spectrographic.

In any method for the determination of thorium, adequate provisions must be made for its separation from other elements, of which titanium, zirconium and rare earths are particularly troublesome. In addition, a suitable means of measurement is required for quantities of thorium less than a milligram. The problem is complicated by the variety of materials to be analyzed. Most of the samples are shales and phosphorites, but igneous rocks and metallic and non-metallic ores must also be considered. The high phosphate content of some samples (up to 35% P_2O_5) is a particularly troublesome factor. The methods found in the literature were found wanting in one or more respects.

These methods are outlined, with some discussion, by Hillebrand and Lundell.[1] The thiosulfate [2] and peroxide [3] separations fail in the presence of phosphate. The precipitation of thorium as fluoride and as iodate are employed by us under conditions modified from those in the literature. Thus, in the iodate method,[4] the acidity recommended in the literature is too high for complete precipitation of small amounts of thorium.

The precipitation of thorium as oxalate has been one of the most generally used methods. Preliminary experiments with very small amounts of thorium gave incomplete recoveries when precipitation was made from 0.3% HCl solution saturated with oxalic acid, although lanthanum was added as carrier. It has been suggested to us [5] that complete elimination of free mineral acid by evaporation of the oxalic acid solution might give better recovery. This has not been tried, as the fluoride method, developed meanwhile, has the advantage of using as carrier mercury, which is easily removed.

The procedure given below is complex and slow. However, it can be simplified considerably for the analysis of less complex materials than those dealt with by us.

ACKNOWLEDGEMENTS

Our work has been greatly aided by discussions with and suggestions by our colleagues J. J. Fahey, Michael Fleischer, M. D. Foster and W. G. Schlecht, and by spectrographic analyses by J. C. Rabbitt. Miss Foster also obtained the transmittancy data for p-dimethylaminoazophenylarsonic acid used in the estimation

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[1] Hillebrand, W. F., and Lundell, G. E. F. Applied inorganic analysis, pp. 416-425. John Wiley and Sons. New York. 1929.

[2] Fresenius, R. and Hintz, E., Z. anal. Chem. 35, 525 (1896).

[3] Wyrouboff, G. and Verneuil, A., Compt. rend. 126, 340 (1898).

[4] Meyer, R. J., Z. anorg. Chem. 71, 65 (1911).

[5] Private communication from Dr. C. J. Rodden, National Bureau of Standards.

of thorium. Michael Fleischer and W. G. Schlecht critically reviewed the manuscript and Schlecht tested the procedure.

OUTLINE OF PROCEDURE

The essential features of the method are:

1) Complete decomposition of the sample. It is considered unsafe to assume that no thorium is present in undecomposed material.
2) Precipitation of thorium phosphate using zirconium or titanium as carrier, the precipitation being made at an acidity of 0.3 N HCl. (Separation from the bulk of constituents.)
3) Concentration of thorium as fluoride by two treatments with hydrofluoric acid, mercurous chloride being used as carrier. (Separation from Ti, Zr, Fe.)
4) Solution of the thorium fluoride in sulfuric acid.
5) Precipitation as thorium iodate. (Separation from traces of rare earths.)
6) Estimation of thorium (a) nephelometrically as the iodate or, (b) photometrically with p-dimethylaminoazophenylarsonic acid or (c) gravimetrically with ammonia and hydrogen peroxide.

DISCUSSION OF PROCEDURE

Separation.

The sample is completely decomposed and a hydrochloric acid solution of the sample is made. Use of sulfuric acid or bisulfate fusions in preparing the solution is avoided if much calcium is present, as with phosphate and carbonate rocks, because any calcium sulfate precipitated will interfere with the isolation of thorium. Any insoluble products, such as hydrolytic precipitates of Ta, Cb, Sn, Ti, Zr, W, especially in the presence of phosphate, will carry down thorium and so must be kept with the solution during the analysis, or if filtered off should be combined with the phosphate precipitate when it is burned (Procedure, section 7).

The phosphate precipitation (Procedure, section 5) is made in 0.3 N hydrochloric acid solution. Under these conditions thorium is coprecipitated with zirconium or titanium phosphate. The precipitate will contain thorium phosphate, zirconium phosphate, titanium phosphate and more or less iron phosphate. Thorium is separated from moderate amounts of rare earths by this treatment (see Experiments, II). If the rare earth content exceeds about 10 mg. of oxides, some rare earth phosphate may be coprecipitated. Depending upon what constituents are present in the sample, there may be no coprecipitation of rare earths even when 30 to 40 mg. are present.

If the sample is known to contain moderate amounts of heavy metals it is best to make an acid H_2S separation before making the phosphate precipitation.

The phosphate precipitate is burned and treated with hydrofluoric acid to dissolve the phosphates of zirconium, titanium and iron, and all the hydrolytic precipitate. Thorium is converted to the insoluble fluoride; mercurous chloride is precipitated from the solution to serve as a bulky carrier for the very small thorium fluoride precipitate. Various other carriers that were tried occluded titanium and zirconium; thus with calcium fluoride, as much as 6% of the zirconium added was coprecipitated. It was hoped that sodium fluoride would inhibit the precipitation of zirconium by stabilizing the fluozirconate ion, but we found that the coprecipitation of zirconium with the calcium fluoride was greatly increased by the addition of sodium fluoride (see Experiments, III). The amount of zirconium and titanium carried down by mercurous chloride is less than 0.01 mg. of each as found by spectrographic analyses (see Experiments, IV). The ease of filtration of mercurous chloride and its easy removal are further advantages.

Sometimes the precipitate of mercurous chloride darkens. This is probably because minute amounts of platinum, or possibly gold, palladium, selenium, tellurium, and arsenic reduced to the elemental condition on the surface of the mercurous chloride. (See Pierson, G. G., Ind. Eng. Chem. Anal. Ed. 6, 437 (1934).)

The mercurous chloride is volatilized, leaving the concentrate of thorium fluoride in the crucible. Great caution is needed to avoid loss of thorium by dusting, both while burning and wetting the fluffy residue. It is also important that the thorium fluoride not be heated so highly as to form less easily soluble thorium dioxide. The usual precautions must be taken against mercury poisoning. A second precipitation as thorium fluoride ensures the removal of the last traces of titanium and zirconium; the residue then contains little impurity besides possibly lead fluoride and some rare earth fluorides or oxides.

The thorium fluoride is converted to sulfate, any ceric ion formed in the ignition of the fluoride precipitate being reduced by addin g sulfurous acid. Any lead present is precipitated and filtered off. The excess sulfuric acid is then removed because it interferes with the precipitation of thorium iodate. In removing free sulfuric acid care must again be taken to prevent the formation of thorium dioxide by overheating.

The thorium sulfate is dissolved in nitric acid, and the thorium separated from any remaining traces of rare earths by precipitation as thorium iodate. It may be directly determined nephelometrically or further treated and determined photometrically with p-dimethylaminoazophenylarsonic acid, or gravimetrically as thorium dioxide.

The photometric method of determination has the advantages of greater objectivity and reproducibility than the nephelometric method, but the latter is simpler and more direct. However, the stability of the cloud of thorium iodate may be markedly affected by the presence of small amounts of impurities. For example, a few tenths of a milligram of zirconium causes very rapid clotting of the iodate precipitate, leading to low results nephelometrically.

Another possible procedure at this point consists of coprecipitation of the thorium with alumina or beryllia, followed by spectrographic determinations. Preliminary experiments indicate the feasibility of this procedure; further work is in progress.

The iodate precipitation may not be necessary for samples containing less than 10 mg. of rare earth oxides (see Experiments, II). The thorium may then be determined directly by the photometric method by adjusting the acidity and adding p-dimethylaminoazophenylarsonic acid. Other such simplifications and shortened procedures will occur to the analyst dealing with materials of more restricted composition than those provided for here.

Determination as thorium iodate.

The cloud of thorium iodate is stable enough for nephelometric estimation up to 0.7 mg. ThO_2, and there is a good spread from none to 0.3 mg. ThO_2. A drop of hydrogen peroxide is added to insure against the presence of quadrivalent cerium, which would also precipitate as iodate. If the sample contains large amounts of rare earths, the thorium may have to be further purified by dissolving the iodate in nitric acid and reprecipitating as the iodate. Experiments with 0.1 mg. ThO_2 and cerous nitrate equivalent to 40 mg. CeO_2 (the largest quantity tried) showed little if any cerium iodate precipitated with the thorium iodate. This quantity of cerium, however, accelerates the clotting of the thorium iodate when the thoria present is about 0.3 mg. ThO_2. If there is any extensive clotting of the thorium iodate in thirty minutes, the safe procedure is to filter off the thorium iodate, dissolve it in nitric acid, and reprecipitate with iodate, in which case the cloud will be stable.

Determination with p-dimethylaminoazophenylarsonic acid.

The precipitation of thorium by p-dimethylaminoazophenylarsonic acid is quantitative only from buffered solutions such as acetate solutions. The acidity must be controlled (see Experiments, V). The reagent is not very specific, as it precipitates to some extent many elements (such as Zn, Ti, rare earths, U, Fe) at this acidity. However, the thorium obtained by the procedure has been freed from interfering elements.

The iodate precipitate is dissolved in HCl and the solution evaporated. Strong oxidizing agents that are released would disturb the photometric determination and are here removed by sulfurous acid. (See Experiments, VI.) The acidity is adjusted and the thorium is precipitated by the dye. The precipitate is filtered and washed to remove excess dye. This arsonic acid precipitate of thorium could be ignited to thorium dioxide and weighed. For photometric determination, the precipitate is decomposed on the filter with dilute NaOH solution, releasing dye equivalent to the amount of thorium in the precipitate. The relation between the amount of dye precipitated with the thorium and the amount of thorium present is exact and reproducible. (See Nazarenko, V. A. J. Applied Chem. USSR 10, 1696 (1937) and Hayes, W. G. and Jones, E. W., Ind. Eng. Chem., Anal. Ed. 13, 603 (1941) for other applications of p-dimethylaminoazophenylarsonic acid in colorimetric work.)

The dye solutions closely follow Beer's Law up to about 0.45 mg ThO_2, and the standard curve is reproducible for even larger amounts (see Experiments, VIII). If the weight of thoria exceeds 0.5 mg, it is better to dilute so that the sample is in the range of Beer's Law.

We found that the commercial p-dimethylaminoazophenylarsonic acid reagent is likely to be inhomogenous; not only does it vary from lot to lot, but different parts of the same lot may vary in composition. A new standard reference curve should be made with every new solution of the arsonic acid reagent, even when successive batches are made from the same bottle of reagent (see Experiments, IX). The experiments show that if the dye is not completely dissolved, the residue differs in composition from the material in solution.

Gravimetric determination.

If the thoria content exceeds 1 mg, as indicated by the size of the iodate precipitate, the iodate precipitate is dissolved in hydrochloric acid and the thorium precipitated with ammonia in the presence of hydrogen peroxide. The precipitate is filtered and ignited to ThO_2. The peroxide provides a delicate test for the presence of rare earths. If the precipitate shows discoloration, it is best to filter without washing, redissolve in nitric acid and reprecipitate as iodate.

PROCEDURE

The chemical concentration of thorium

Reagents: Hydrochloric acid (1 + 1)

Hydrochloric acid (7 + 100)

Nitric acid (1 + 1)

Sulfuric acid

Sulfuric acid wash solution (1 + 100)

Hydrofluoric acid

Sulfurous acid, 6%

Zirconium nitrate, 5 mg ZrO_2 per ml

Diammonium hydrogen phosphate $(NH_4)_2HPO_4$

Ammonium nitrate wash solution, 4%

Potassium iodate, 7-1/2% solution

Mercurous nitrate solution, 8 mg HgCl equivalent per ml

Dissolve 0.952 g of reagent grade mercurous nitrate in water containing a few drops of nitric acid and make to 100 ml with water.

Filters: S & S 589 white label, 11 cm

Whatman 40, 9 cm

Whatman 42, 7 cm

Filter paper pulp

1. For samples containing less than 0.04% Th, take 5.00 g, proportionally less for samples of higher Th content. Prepare a hydrochloric acid solution of the sample as outlined in Geological Survey Trace Elements Project Report No. 2. Any hydrolytic precipitate should be left in the solution, or if filtered should be added to the phosphate precipitate when it is burned (Procedure, section 7).

2. Evaporate the solution to dryness to eliminate the free acid.

3. With a pipette add 10 ml. of (1 + 1) HCl solution. Digest about 5 minutes on the steam bath and then add 130 ml of water. Digest until the soluble salts are dissolved.

4. While stirring, slowly add 10 ml of the zirconium nitrate solution. Warm to about 90°C.

5. Add 4 g of diammonium phosphate dissolved in about 20 ml of water. Dilute with water to 200 ml. Cover the beaker and digest on the steam bath for at least 4 hours.

6. Add paper pulp, stir, and filter on a 11 cm S & S 589 white ribbon filter paper. Wash with 4% NH_4NO_3 solution.

7. Transfer the filter paper with precipitate to a porcelain crucible. Burn gently, starting at a low heat and gradually raising the temperature, until the carbon is burned off.

8. Transfer the residue to a 100 ml platinum dish or crucible. Moisten with a little water and add 20 ml of HF. Cover with a platinum cover and digest until the precipitate is in solution. Evaporate on the steam bath until about 8 ml. remain. Add 10 ml. of HF and evaporate again to about 8 ml. Dilute with 30 ml of water. Warm on the bath.

9. Add 10 ml of the mercurous nitrate solution. Next add 1 ml of dilute HCl (7 + 100) and stir with a platinum rod. Warm on the bath for a few minutes and then allow to stand at room temperature for about 4 hours.

10. Filter on a No. 40 Whatman 9 cm filter in a hard rubber funnel and wash twice with 10 to 15 ml of approximately 5% HF wash solution, making the wash solution directly in the dish that contained the precipitate and scrubbing the inside of the dish thoroughly with a rubber policeman wetted by the solution. Wash twice with water.

11. Transfer the paper and precipitate to a 20 ml platinum crucible, shield from drafts and burn gently below 500°C in a well-ventilated hood until the paper is burned off and the HgCl volatilized. The precipitate must be burned carefully and slowly; if the mercurous chloride is volatilized roo fast, thorium may be lost by dusting. Burning at too high a temperature may convert some of the thorium fluoride to ThO_2 which is harder to dissolve.

12. Carefully moisten the fluoride residue with a few drops of water. Add about 8 ml. of HF. Cover the crucible and digest on the steam bath for 20 minutes. Transfer the contents of the crucible to a platinum dish. Wet and scrub the inside of the crucible thoroughly with a rubber policeman, rinsing into the dish. Dilute with water to 40 ml. Add 10 ml. of mercurous nitrate solution, warm, add 1 ml of dilute HCl (7 + 100) solution and stir. Let stand at room temperature for about 4 hours.

13. Filter on a No. 40 Whatman 9 cm filter paper in a hard rubber funnel and wash twice with HF wash solution and twice with water.

14. Transfer the paper and precipitate to a small (20 ml) platinum crucible and again carefully burn at below 500°C in a well-ventilated hood until the paper is burned off and the HgCl is volatilized.

15. Carefully wet the residue in the crucible with a few drops of water; dry on the steam bath.. Carefully add 0.5 ml of H_2SO_4. Fume on the hot plate for about 15 minutes, keeping the crucible covered. Cool. Cautiously add water until the crucible is about three-fourths full. Add a few drops of 6% sulfurous acid solution to decolorize any quadrivalent cerium, and evaporate until water is removed. Bring to fumes of sulfúric acid and fume 15 minutes. Cool. Add about 10 ml of water and transfer the contents to a 50 ml beaker. Police the crucible and wash with water, adding the washings to the beaker. At this point, the volume of the solution should be 25 to 30 ml. Warm gently, then allow to stand for about 4 hours.

The dilution with water and the fuming with sulfuric acid should be repeated a third time if the amount of thorium is large, or if the final insoluble residue is large.

16. Filter off any lead sulfate on a No. 42 7 cm Whatman paper and wash a few times with 1% H_2SO_4 solution. Collect the filtrate in a 50 ml platinum dish.

17. Evaporate the solution nearly to dryness and then bring to fumes. Drive off all the free sulfuric acid at a low temperature. This is conveniently done by heating on a hot plate until dry and then rotating the dish above a low Bunsen flame until no more fumes appear. The temperature should be kept below 450°C to avoid formation of ThO_2, which in the next step may not dissolve completely in the nitric acid. The removal of free sulfuric acid is essential since excess sulfate interferes with the precipitation of thorium iodate (section 19).

18. Add from a pipette 6 ml of (1 + 1) HNO_3 solution. Add 1 drop of 30% hydrogen peroxide. Warm gently and then add 10 ml of water. Cover the dish and digest on the steam bath for a few minutes until the thorium is dissolved.

19. Transfer with a jet of water to a 100 ml beaker, policing the dish thoroughly. Adjust the volume to 42 ml with water. Cool to room temperature. Add by pipette 8 ml of 7 1/2% KIO_3 solution. The thorium is now determined either (a) nephelometrically as the iodate when less than 1 mg ThO_2 is present (section 20) or (b) photometrically with p-dimethylaminoazophenylarsonic acid (section 21) or (c) gravimetrically as oxide if more than 1 mg ThO_2 is indicated by the size of the iodate precipitate (section 28).

The estimation of thorium

Method A. Nephelometrically as the iodate

20. Let the thorium iodate precipitate stand 15 minutes (30 minutes for ThO_2 content of .1 mg or less) and compare against a series of standards containing known amounts of thorium with the same amounts of nitric acid and iodate in the

same volume, and prepared at the same time as the unknown sample.

If the iodate precipitate indicates a thorium content greater than 0.3 mg ThO_2 and less than 1 mg ThO_2, an aliquot is taken in this way. Add 12 ml of (1 + 1) nitric acid solution to dissolve the thorium iodate. Take a one-third aliquot into another 100 ml beaker. Adjust the volume with water to 45 ml and add 5 1/3 ml of 7 1/2% KIO_3 solution from a graduated pipette. Match against a series of standards. The match is made by placing the beakers on a dark plate in front of a window and looking down into the beakers.

Method B. Photometrically with p-dimethylaminoazophenylarsonic acid

Reagents: Ammonium hydroxide

Sulfuric acid

Sulfurous acid, 6%

Hydrochloric acid, concentrated

Hydrochloric (1 + 1)

Hydrochloric acid (7 + 100)

Sodium hydroxide solution, 4%

Methyl red indicator, 0.1% solution in alcohol

P-dimethylaminoazophenylarsonic acid solution. Dissolve 0.1 g of the finely powdered reagent in 50 ml of (1 + 1) alcohol solution containing 10 g of ammonium acetate. Filter.

Buffered wash solution. Dissolve 10 g ammonium acetate and 12 ml of (7 + 100) HCl solution in 488 ml of water.

Filters: Whatman 42, 7 cm

Asbestos Gooch filter, 10 ml

21. Let the thorium iodate precipitate stand overnight. Filter on a 7 cm No. 42 Whatman paper. Do not wash.

22. Dissolve the iodate precipitate off the filter with alternate washes of hot

(1 + 1) HCl solution and hot (7 + 100) HCl solution, three portions of each. Catch the filtrate in the same 100 ml beaker that contained the iodate precipitation.

23. Evaporate to dryness on the bath. Add about 8 ml of fresh 6% sulfurous acid and evaporate to dryness again.

24. Take up in 4 drops of HCl and 43 ml of water. Add 2 drops of methyl red indicator and neutralize with ammonia until the methyl red turns yellow. Now add dropwise a solution of HCl (7 + 100) until the methyl red just turns red. Add 1.2 ml excess. Now add 5 ml of a solution of p-dimethylaminoazophenylarsonic acid. Cover the beaker and allow to digest on the steam bath until the precipitate clots (10 to 20 minutes).

25. Filter on a 10 ml asbestos Gooch filter and wash 4 times with 10 ml portions of the ammonium acetate wash solution.

26. Pour over the Gooch filter 30 ml of a warm 4% solution of sodium hydroxide and catch the washings in a clean receiver. Wash once with water.

27. Make the filtrate up to 250 ml. Read the percent transmittancy on an electrophotometer at a wave length of 425 millimicrons, or on a spectrophotometer at 460 millimicrons. (See Experiments, VII.) Obtain the mg thoria equivalent by reference to a standard curve. (See Experiments, VIII.)

If there is more than 0.5 mg ThO_2, it is better to make the dilution so that the sample is in the ranges of Beer's Law. The standard curve should be checked at intervals; two known concentrations usually are enough.

Method C. Gravimetrically with ammonia and peroxide

28. If the thoria content exceeds 1 mg, the determination is made gravimetrically. Allow the iodate precipitate (section 19) to stand overnight. Filter on a 7 cm. No. 42 Whatman paper, but do not wash. Dissolve the iodate precipitate off the filter with alternate washes of hot (1 + 1) HCl solution and hot (7 + 100) HCl solution, three portions of each. Catch the filtrate in the same 100 ml beaker that contained the iodate precipitate. Evaporate the solution to dryness. Add

5 drops of HCl and 15 to 20 ml of water. Warm. Add 1 drop of 30% H_2O_2 and then neutralize with ammonia, adding a few drops of ammonia in excess. Digest on the steam bath about 15 minutes, add paper pulp and filter on a No. 40 7 cm Whatman paper. Wash with 4% ammonium nitrate solution. Ignite to ThO_2 and weigh.

EXPERIMENTS

I. Analysis of synthetic mixtures

The methods described above were tested by analysis of solutions whose thorium content was not known to the analyst. The standard thorium solution was made from reagent grade thorium nitrate that was found spectrographically to contain less than 0.1% of any other metal. The solution was standardized by evaporating to dryness and igniting to oxide, and by precipitating with ammonia and peroxide and igniting to oxide.

The solutions for analysis were made by adding various amounts of thorium nitrate to 50 ml of either of two stock solutions. All reagents used were evidently free enough from thorium for the purpose, because the results with solutions of the lowest thorium contents analyzed were not significantly higher than the amount of thorium added. One of the synthetic stock solutions, Solution S, was made to represent the composition of shales (omitting the silica), the other, Solution P, was made to represent the composition of phosphate rock. Fifty ml of solution S and P contain the following:

	Solution S	Solution	Salt used
Al_2O_3....................	0.75 g	0.20 g	aluminum chloride
Fe_2O_3....................	.50 g	.20 g	ferric chloride
MgO....................	.05 g	.05 g	magnesium chloride
CaO....................	.50 g	1.50 g	calcium chloride
K_2O....................	.30 g	.20 g	potassium chloride
TiO_2....................	.05 g	.05 g"	titanium tetrachloride
ZrO_2....................	.005 g	.005 g"	zirconium nitrate
V_2O_5....................	.02 g	.02 g	ammonium metavanadate
Cr_2O_3....................	.02 g	.02 g	potassium dichromate
MoO_3....................	.005 g	.005 g	ammonium molybdate
MnO....................	.005 g	.005 g	manganese chloride
BaO....................	.005 g	.005 g	barium chloride
PbO....................	.005 g	.005 g	lead carbonate

	Solution S	Solution P	Salt used
P_2O_5	.010 g	1.25 g	ammonium phosphate
Y_2O_3	.005 g	.01 g*	yttrium nitrate
CeO_2	.005 g	.01 g*	cerous nitrate
NiO	None	.005 g	nickel chloride
As_2O_5	None	.005 g	sodium arsenate

* These were added separately just before the analysis was begun

Table 1 gives the analytical results obtained.

Table 1. Analyses of synthetic mixtures

Sample No.	Type sample	ThO_2 taken	ThO_2 found nephelometrically	ThO_2 found photometrically	ThO_2 found gravimetrically
		mg	mg	mg	mg
P2	S	0.05	0.07	0.07	....
P3	P	.10	.09	.10	....
P4	S	.25	...	.26	....
P6	S	.30	.27	...	....
Q4	S	.30	.20	.23	....
Q7	P	.50	.70	.66	....
P1	P	.55	.55	...	....
M1	P	.60	.66	...	....
J2	S	.70	.80	...	....
Q2	S	.90	1.0	.80	1.1
P4	S	.90	.70	...	....
H2	P	.95	1.1	...	....
Q1	P	1.00	1.0	.87	....
J6	S	1.10	...	1.04	....
Q8	S	1.60	...	...	1.5
Q5	P	1.70	...	...	1.9
J4	P	1.80	...	...	1.9
Q3	S	3.30	...	...	2.6
Q6	P	5.40	...	...	5.2

The procedures were further tested by analyses by W. G. Schlecht of eight synthetic mixtures. The results are given in Table 2 to indicate what might be expected on a first trial of the method by an ~~only~~ analyst unfamiliar with the procedures. We think ~~think~~ that the discrepancies in the photometric results for samples E6 and E5 are caused mainly by imperfect separation of zirconium, which can cause small positive or negative errors in the nephelometric determination and larger positive errors in the photometric determination.

Table 2. Analyses of synthetic mixtures

Sample No.	Type sample	ThO_2 taken	ThO_2 found nephelometrically	ThO_2 found photometrically	ThO_2 found gravimetrically
		mg	mg	mg	mg
S6	P	0.00	0.18	0.52	....
S1	S	0.10	0.10	....	....
S3	P	0.25	0.3	....	....
S8	S	0.40	0.35	....	....
S5	P	0.65	0.7	1.05	
S7	S	0.80	0.6	0.65	
S4	P	1.20	> 1.0	1.25	....
S2	S	1.45	...	....	1.40

II. Occlusion of rare earths with the phosphate precipitate

To 50 ml of solution P, which contains 10 mg Y_2O_3 and 10 mg CeO_2, 0.95 mg (A), 0.25 (B) and 0.6 mg (C) of ThO_2 were added. These were analyzed according to the procedure through section 16. Precipitation with excess ammonia in the presence of a few drops of 30% H_2O_2 gave these weights when ignited.

(A) 3.4 mg

(B) 2.3 mg

(C) 2.5 mg

The ignited oxides were dissolved and the thorium content determined nephelometrically as the iodate. The thorium contents found were:

(A) 1.1 mg ThO_2

(B) .36 mg ThO_2

(C) .66 mg ThO_2

Sample (A) showed therefore 2.3 mg of rare earth oxides occluded

Sample (B) .... 1.9 ....Do.......................

Sample (C) .... 1.8 ....Do.......................

When the experiments were repeated with solution S that contained only half the amounts of rare earths in solution P, no rare earths were found to accompany the thorium.

III. Failure of HF separation of thorium from zirconium in the presence of alkaline earths and alkalies

To each of four platinum dishes was added 50 mg of ZrO_2 as the phosphate, .3 mg ThO_2 as the nitrate and 60 mg CaCl2. The mixtures were evaporated to dryness and 20 ml of HF solution was added to each. After digestion the solutions were evaporated to 8 ml and then 10 ml of HF added. The solutions were evaporated again to 8 ml and then diluted with water to 50 ml and allowed to stand at room temperatur for 4 hours. They were then filtered and washed with 4% HF solution. The residues were burned in platinum and dissolved by fuming with perchloric acid. The solutions were diluted with water and exactly 100 mg of Al_2O_3 (as the chloride) was added to each. Ammonia was now added until the solutions ~~were~~ were neutral to methyl red and the precipitates obtained were ignited and weighed. The weights of the ignited precipitates were .1316, .1312, .1285, .1311 g. The excess of about 30 mg was found to be due to zirconium.

In another series, 0.5 g sodium fluoride was added in addition to calcium in hope of fixing the fluozirconate ion, but the results were worse since about 10% of the final ignited precipitate was ZrO_2.

IV. Non-occlusion of zirconium, titanium, and iron by thorium fluoride when mercurous chloride is used as carrier

To each of four beakers was added 50 mg ZrO_2 as the nitrate, 50 mg TiO_2 as the chloride, 1 g Fe_2O_3 as the chloride, and 0.5 mg ThO_2 as the nitrate. A phosphate precipitation was made according to the procedure outlined in section 5. After filtration, the phosphate precipitates were burned and treated with HF, as in section 8.

The ThF_4 was filtered off with the aid of 80 mg of mercurous chloride as carrier. The fluoride precipitate was dissolved with fuming sulfuric acid, exactly 100 mg of Al_2O_3 was added and an ammonia precipitation made. This was filtered off, burned and examined spectrographically by J. C. Rabbitt for zirconium, titanium and iron. The results obtained with only 1 HF treatment were:

No.	TiO_2	ZrO_2	Fe_2O_3
1	0.01	0.01	0.008
2	0.008	0.006	0.005
3	0.02	0.005	0.006
4	0.008	0.01	0.005

V. Optimum conditions for the ~~precipites~~ precipitation of thorium with p-dimethylaminoazophenylarsonic acid

Effect of acid concentration.

To each of six beakers was added a solution of thorium nitrate equivalent to .4 mg ThO_2, 0.2 ml of HCl, 1 g of ammonium acetate, and distilled water to make the volume to 43 ml. Ammonia was next added until the solutions were alkaline to methyl red. Dilute (7 + 100) ~~HCl~~ HCl was then added dropwise until the solutions were just acid to methyl red, followed by a known excess of dil. HCl (7 + 100). Five ml of a saturated solution of p-dimethylaminoazophenylarsonic acid in alcohol was then added to each to precipitate the thorium. After digestion on the steam bath for 15 minutes, the thorium precipitates were filtered on Gooch crucibles and washed 4 times with 10 ml portions of ammonium acetate wash solution. The precipitates were dissolved off the Gooch crucibles with 30 ml of 4% NaOH and the filtrate made to 250 ml. The solutions were then read in the electrophotometer. The readings obtained are listed below.

	Electrophotometer reading
1) Just acid to methyl red	21
2) 0.1 ml 7% HCl/past 1.......	38
3) 0.7 ml .....Do..........	54
4) 1.2 ml .....Do..........	55
5) 3 ml ....Do..........	57
6) 6 ml ....Do..........	90

The results ~~carried~~ obtained show that the acidity is important and must be controlled. The optimum acidity taken is that given by a solution containing 1 g of ammonium acetate and 1.2 ml of (7 + 100) hydrochloric acid in a total volume of 50 ml.

Effect of concentration of p-dimethylaminoazophenylarsonic acid.

Using the optimum acidity, the amount of p-dimethylaminoazophenylarsonic acid was varied in two tests. Using 2.5 ml of the arsonic acid reagent, the color reading obtained was 52.5 using 10 ml of the arsonic acid reagent, the reading was 57.5.

The concentration of p-dimethylaminoazophenylarsonic acid used in the precipitation of thorium is evidently not important. The small discrepancy noted above is probably because the precipitate was washed four times in each experiment, so that washing was probably not complete for the more concentrated solution. We never try to wash all excess dye from the precipitate. Four washings are enough for practical purposes when 5 ml of reagent is used.

VI. Interferences of oxidizing agents in the photometric determination of thorium

Various amounts of thorium were precipitated as the iodate as in the procedure (section 19). The precipitates were filtered 24 hours later, dissolved off the filter with 25 ml of (1 + 1) HCl and the paper washed with water. The solutions were evaporated to dryness, taken up with 4 drops of HCl and 42 ml of water. The photometric procedure was then applied for the estimation of thorium. The results obtained are given below.

ThO_2 taken mg	ThO_2 found photometrically mg	% Recovery
0.15	0.135	90
.40	.37	92
.75	.67	90
1.4	1.23	88

The above experiments were repeated except that after the HCl ~~solution of~~ solution of the iodate was evaporated to dryness, 8 ml of 6% sulfurous acid was added and the solution again evaporated to dryness. The residue was taken up with 4 drops of HCl and 42 ml of water and the thorium estimated photometrically. The results given below show excellent recoveries:

ThO_2 taken mg	ThO_2 found photometrically mg
0.15	0.155
.40	.395
.80	.80
1.40	1.41

VII

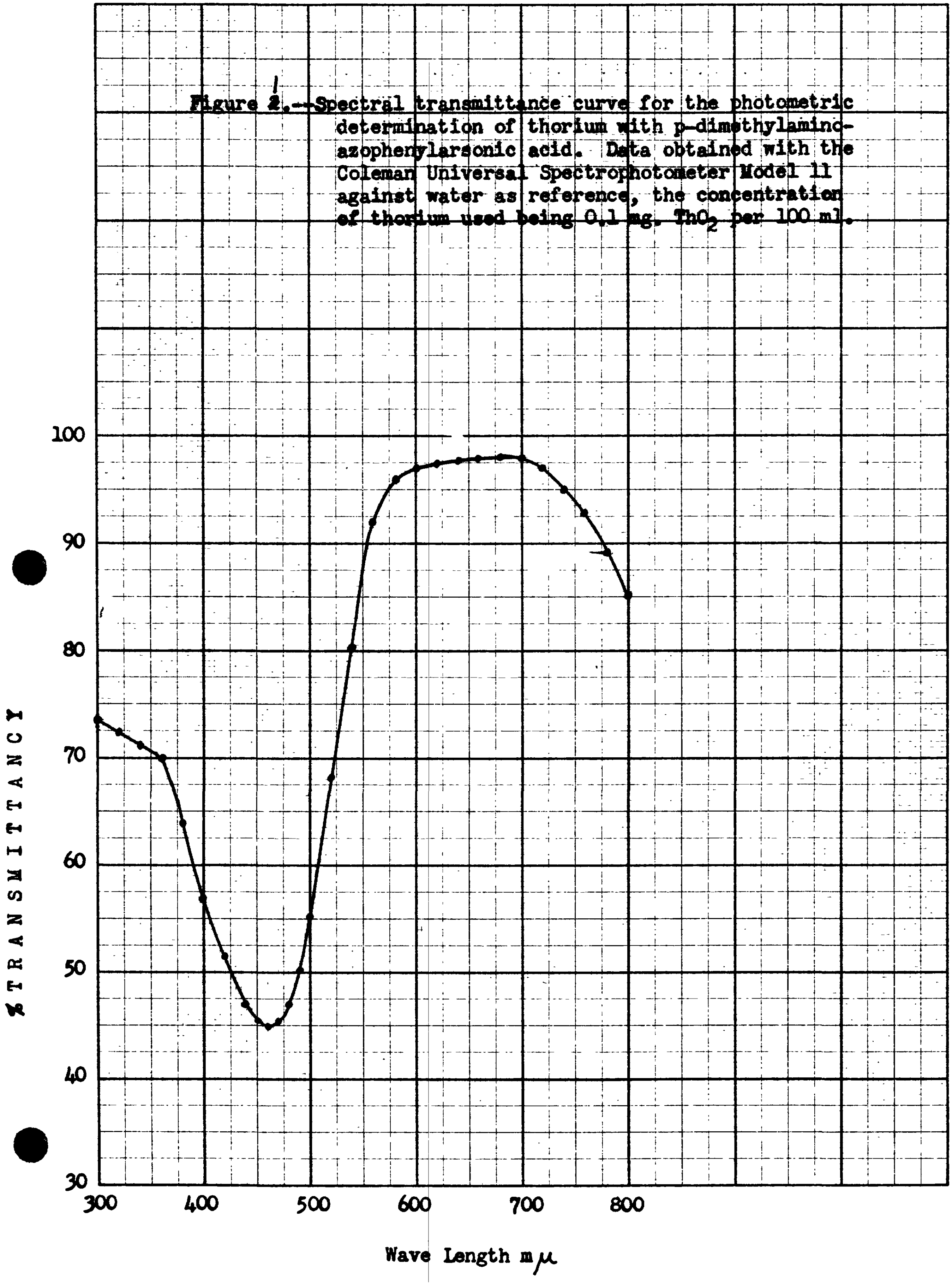

Figure ~~2~~ 1.--Spectral transmittance curve for the photometric determination of thorium with p-dimethylaminoazophenylarsonic acid. Data obtained with the Coleman Universal Spectrophotometer Model 11 against water as reference, the concentration of thorium used being 0.1 mg. ThO_2 per 100 ml.

VIII. Standard curve for the photometric determination of thorium with p-dimethylaminoazophenylarsonic acid

Using the procedure outlined in section 24 through 27, the electrophotometer readings for different amounts of thorium are given below. The data were obtained with a Fisher electrophotometer using a 425 millimicron filter.

ThO_2 mg	Electorphotometer reading
0.10	14.5
.20	29.0
.30	43.3
.40	56.5
.50	67.5

Figure 2 gives a plot of the results.

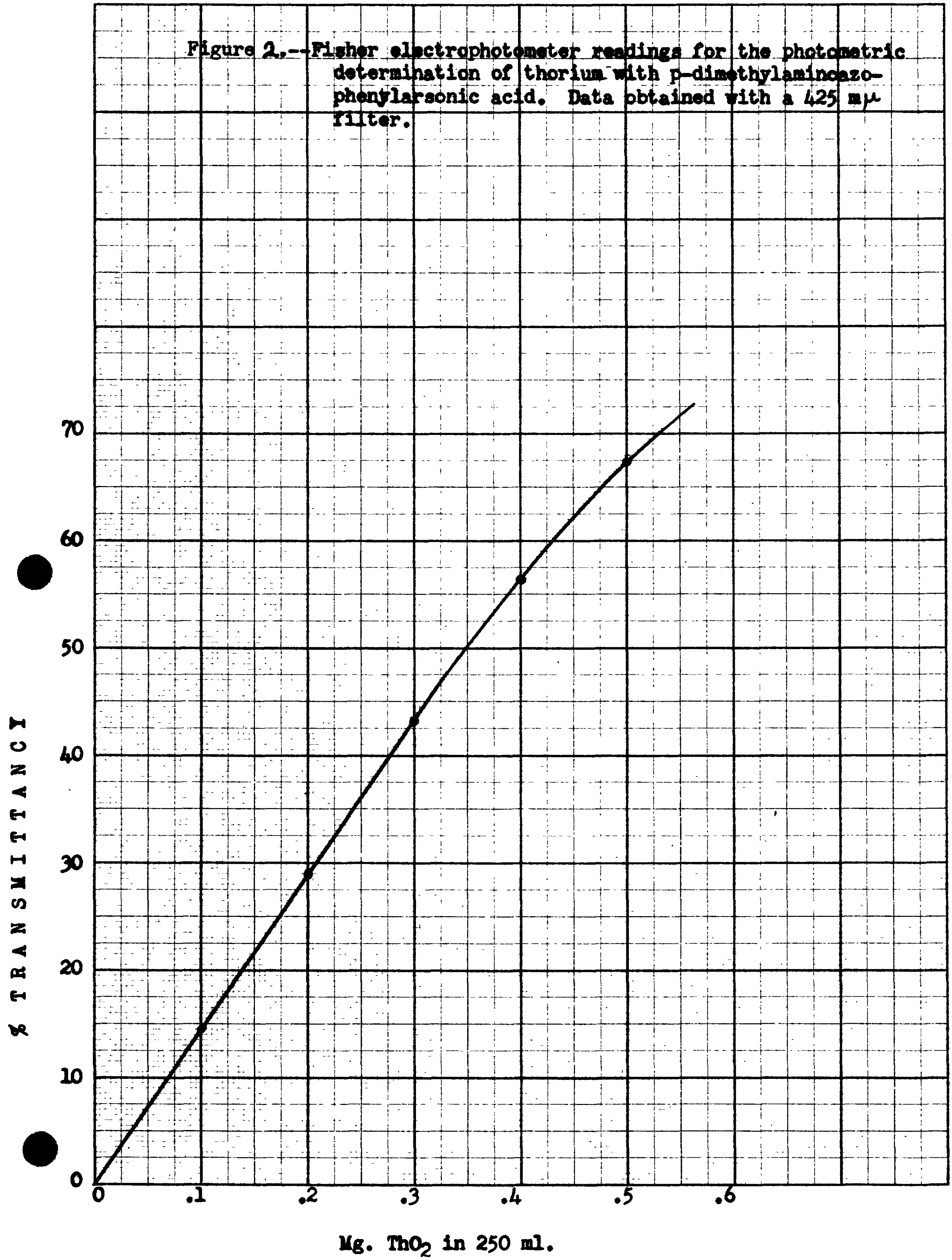

Figure 2.--Fisher electrophotometer readings for the photometric determination of thorium with p-dimethylaminoazophenylarsonic acid. Data obtained with a 425 mμ filter.

IX. Inhomogeneity of the reagent p-dimethylaminoazophenylarsonic acid

Two saturated alcoholic solutions of the reagent were made in this way;

1) Excess of p-dimethylaminoazophenylarsonic acid was digested with alcohol to make a saturated solution. Excess reagent was filtered from the solution which was labelled No. 1.

2) The excess reagent obtained in the paper from (1) was treated with more alcohol to form a second saturated solution. This was filtered and labelled No. 2.

Various amounts of thorium were determined photometrically using the optimum conditions of excess acid and ammonium acetate, using alcoholic solutions Nos. 1 and 2 for precipitation. The electrophotometer readings obtained are given below;

ThO_2 taken mg	Electrophotometer reading Solution 1	Solution 2
0.15	17	21
.30	34	42
.45	50	58
.60	64	73

Both solutions follow Beer's law up to about 0.4 mg ThO_2, but they do not give the same reading for the same amount of thorium.

In another experiment, 2 g of p-dimethylaminoazophenylarsonic acid was ground to an impalpable powder in an agate mortar. Three 0.1 g portions were weighed and to each were added 10 g of ammonium acetate, 25 ml water and 25 ml of alcohol; they were warmed until solutions were obtained. This made three identical dye solutions. The results obtained when .4 mg ThO_2 was determined photometrically by each solution are given below.

ThO_2 taken mg	Electrophotometer reading	Reagent solution used
.4	60	5 ml of #1
.4	60	5 ml of #2
.4	60	5 ml of #3

Consistent results will therefore be obtained if a complete solution of thoroughly mixed reagent is used.