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COLORIMETRIC DETERMINATION OF PLUTONIUM IN MICROGRAM QUANTITIES

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COLORIMETRIC DETERMINATION OF PLUTONIUM IN MICROGRAM QUANTITIES

by

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ABSTRACT

A method has been developed for the determination of plutonium over the range 5 to 100 μg with an accuracy of ±1% at the 100 μg level. The coloured complex between tetravalent plutonium and the commercial reagent Thoronol [1 - o - arsenophenyl azo) - 2 napththol - 3 - 6 - disulphonic acid] is measured on a Spekker Absorptiometer. This can be used to estimate the amounts of the three, four and six valent states present in a plutonium sample. The thoronol complexes formed with ferric and uranyl ions have been examined at different acidities. Methods are suggested to remove or to minimise the effects due to most of the complexing cations such as iron or anions such as fluoride.

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Illustrations

1. Introduction

1.1 In 1944 Kusnetsov (1) reported that 1 - (o - arsenophenyl azo) - 2 - napththol - 3 - 6 - disulphonic acid, hereafter called Thoronol formed a specific red precipitate with thorium in hydrochloric acid and described a spot test technique for the detection of thorium. This was later developed by Thomason and co-workers (2) into a method for the determination of thorium on the microgram scale, measuring the coloured complex with Thoronol on a Beckmann Spectrophotometer. Horton (3) in 1952 extended this work to include the spectrophotometric determination of microgram quantities of zirconium. The present report deals with the development of a method for the rapid determination of plutonium in the various valency states on the microgram scale. The method consists of addition of the reagent, adjustment of pH, dilution to 25 mls and measurement of the optical density in a Spekker absorptiometer against a reference solution of the reagent. Ilford 605 filters and 4 cm. absorption cells are used with the Spekker.

2. Experimental

2.1 Colour absorption

The absorption spectra of the solutions were measured using a Unicam S.P. 500 Quartz Spectrophotometer. For the great majority of the measurements, absorption cells of 4 cm. path lengths were used. The solutions were either 0.1 N or 0.25 N in acid and contained 2.5 mls of 0.1% aqueous solution of thoronol reagent, in a final volume of 25 mls before transference to the 4 cm. absorption cells. Measurement of the colour of a water solution of thoronol against water as a blank (Curve A, Fig. 1), and of thoronol plus tetravalent plutonium against water (Curve B, Fig. 1) showed a shift of the absorption band towards longer wavelengths upon the addition of plutonium. Measurement of the solution plus plutonium (100 μg) and reagent against the reagent as blank gave the predicted curve (C, Fig. 1) with a maximum at 540 millimicrons.

2.2 A comparison was made of the relative sensitivity of the Higher Spekker Absorptiometer with the Unicam S.P. 500 Spectrophotometer. This showed (Fig. 2) very little difference in the optical density. Measurements of the optical density of the plutonium/thoronol complex less thoronol blank were made (a) with the Spectrophotometer set at a wavelength of 540 millimicrons, using 4 cm. absorption cells and (b) with the Spekker Absorptiometer using a mercury lamp and an Ilford 605 filter plus 4 cm. cells. Hence, it should now be stressed that the quantities of plutonium in the tetravalent state as measured in a commercial absorptiometer are (i) as small as is possible when using a spectrophotometer for the same measurements and as will be seen from the results in this Report (ii) several hundred times smaller than the quantities required to estimate plutonium to a similar accuracy by estimation of the plutonium absorption spectrum on the spectrophotometer.

TABLE I

OPTICAL DENSITIES OF PLUTONIUM/THORONOL COLOUR PLOTTED AGAINST 0.1% THORONOL REAGENT IN 0.25 NORMAL HNO_3, USING 4 CM. CELLS IN THE SPEKKER ABSORPTIOMETER

Tetravalent Pu solution	Spekker reading
1 microgram Pu per ml. solution	0.196
2 " " " " "	0.390
3 " " " " "	0.575
4 " " " " "	0.773
5 " " " " "	0.950
6 " " " " "	1.10

3. Beer's Law

3.1 It has been observed that this law is obeyed up to an optical density of about unity (see Fig. 2), the density above this point being unreliable, primarily owing to instrument defects. Beer's Law only holds for solutions in dilute nitric or hydrochloric acid. Acids of greater strength also cause the apparent breakdown of Beer's Law, but this is due to attack on the colour complex.

4. Effect of Acidity on the Optical Density and Colour Stability

4.1 There appears to be a small difference in optical density of the plutonium/thoronol complex in the acidity range 0.05 to 1 normal nitric and hydrochloric acid, when the density reading is extrapolated back to zero time. However, the picture is complicated by the effect of the acidity on the stability of the complex. At low acidities (0.25 normal or less) the colour fades much less rapidly than at higher acidities. Hence, measurement of the optical density of the complex at five minutes after the addition of reagent, gives the impressions (i) that the optical density is much less for solutions of higher acidity and (ii) that Beer's Law does not hold at these higher acidities. Fig. 3 shows the apparent effect of acidity at zero plus 5 minutes, Fig. 4a illustrates the fading of the colour of the complex at one of the higher acidities in contrast to Fig. 4b where the complex is stable over half an hour at a low acidity. Results showing the effect of time on the optical densities of the plutonium/thoronol complex at different acidities from 0.05 to 1 normal for both nitric and hydrochloric acid, are given in the Appendix (Tables I - IX).

4.2 Nitric acid also slowly affects the blank thoronol reagent, causing an apparent increase in density of the sample due to slow fading of the blank of about 5 - 10% per hour, and the higher the acidity the quicker

the blank fades. This effect is eliminated by making a fresh blank for each plutonium estimation. The fading does not occur in hydrochloric acid solutions.

4.3 As plutonium solutions are estimated in the tetravalent state, sodium nitrite is often present, and here also there is an apparent increase in optical density of a sample owing to gradual fading of the blank in the presence of nitrous acid. An erroneously high reading is obtained therefore if a fresh sample is measured against an old blank. Also, the peak in the absorption spectrum changes to 526 millimicrons giving a very high reading at 526 and a low reading at 540 millimicrons.

4.4 However all these sources of error can be eliminated by making a fresh blank with each sample, keeping the acidity low and estimating the plutonium within five minutes of its addition to the thoronol reagent.

5. Extinction Coefficients for the Valency States of Plutonium

5.1 The extinction coefficient E is much greater for tetravalent plutonium than for the trivalent or hexavalent form as is illustrated in Table II. These values were all obtained in 0.25 normal hydrochloric acid solution using the S.P. 500 spectrophotometer and estimating at the 540 mμ peak.

TABLE II

Pu Valency	III	IV	VI
E	108	11,000	16

For these optical measurements milligram quantities of the trivalent and hexavalent plutonium were required.

6. Estimation of the three Valency States in the mixture

6.1 It was assumed that no pentavalent plutonium was present at the acidities used in mixtures of the other three valency states. Two mixtures were taken at acidities of 0.25 N HNO_3 and 1.0 N NHO_3 the concentrations being 0.1 mg Pu/ml and 0.5 mgPu/ml respectively.

6.2 These solutions were diluted to suitable concentrations with aqueous acid and the tetravalent plutonium estimated directly on an aliquot via the plutonium/thoronol complex on the Spekker. The optical densities directly attributable to the tri and hexavalent Pu were

neglected. A small quantity of sodium nitrite was added to another aliquot to oxidize the trivalent Pu to the tetravalent state. The optical density thus obtained was a measure of the tri-plus tetravalent plutonium present in the aliquot. To a third aliquot hydroxylamine hydrochloride was added to reduce all the plutonium present to the trivalent state. Ten minutes later, 10% excess sodium nitrite was added to oxidize this plutonium to the tetravalent state. The optical density of this complex was a measure of the total plutonium in the sample. From these three Spekker readings the Pu IV concentration, the Pu III plus Pu IV concentration and the total Pu concentration respectively were obtained. The Pu III and Pu VI concentrations were then found directly by subtraction. These figures were compared with T.T.A. extraction of the original strong Pu solutions using a similar procedure. The plutonium was washed out of the T.T.A./benzene extracts with 10 H HNO_3 and counted on a 50% geometry proportional counter. The results illustrated in Table III show good agreement between the T.T.A./counting method and the colorimetric method and the overall mass balance is good.

TABLE III

	Pu III	Pu IV	Pu VI	Total Pu
Colorimetric Method on diluted samples.	0.0365	0.0404	0.0192	0.096 mgs/ml
T.T.A./counting method on original solutions.	0.0360	0.0392	0.0175	0.093 mgs/ml
Colorimetric method on diluted samples.	0.092	0.350	0.071	0.513 mgs/ml
T.T.A./counting method on original solutions.	0.080	0.340	0.080	0.500 mgs/ml

The original samples were counted on a 50% geometry proportional counter and referred to a standard source. By this means they were found to contain 0.098 mgs Pu/ml and 0.506 mgs Pu/ml.

7. Analytical Procedure

7.1 A standard line is obtained at a definite acidity between 0.05 and 0.25 normal, say 0.1 normal HCl or HNO_3 (see Fig. 2). The standards are made up by adding known amounts of tetravalent plutonium from 0-150 µg to a 25 ml. graduated flask containing 2.5 mls of 0.1% aqueous solution of commercial Thoronol reagent and the contents made up to the mark with the requisite acid. The optical densities of these standards are measured in 4 cm. cells against a reference solution on a Spekker absorptiometer using a mercury lamp and an Ilford 605 filter. The

reference solution or blank is made by adding 2.5 mls. of 0.1% aqueous thoronol reagent to a 25 ml graduated flask and making up to the mark with the requisite acid. An unknown plutonium solution is diluted to a microgram scale concentration and an aliquot placed in a 25 ml. flask as for the standards and measured against the blank. The unknown plutonium concentration is then obtained from the optical density by reference to the standard line.

8. Interfering substances

8.1 A number of tetravalent cations interfere, thorium, zirconium and tetravalent uranium causing the greatest interference as the extinction coefficients of their thoronol complexes are of the same order as that of tetravalent plutonium. Trivalent iron and cerium also interfere but not so badly. Table IV gives a list of the extinction coefficients of these materials in order to illustrate their relative interference. In the case of hexavalent uranium and trivalent iron, as will be seen later, their thoronol complexes do not follow Beer's Law, and so their extinction coefficients (E) quoted are maximum figures. All these E values below are obtained in 0.25 normal acid.

TABLE IV

Cation	Pu(IV)	Th	Zr	U(IV)	Ce(III)	Fe(III)	U(VI)
Extinction coefficient (E)	11,000	16,000	3,000	9,000	23	57	37

NH_4NO_3 also causes interference by decreasing the optical densities of plutonium/thoronol solutions, when in concentrations greater than a thousand times the Pu concentration.

8.2 Anions that complex plutonium also inhibit the formation of the coloured complex. Phosphates, fluorides, oxalates and large concentrations of sulphate interfere and must be removed. Most of these interfering anions and cations can be removed either by diluting out of the interfering range or by using the methods mentioned later in this report.

9. Examination of the Ferric/Thoronol and Uranyl/Thoronol Complexes

9.1 As iron and uranium are the metals most likely to be present in plutonium solutions it was decided to examine them separately with thoronol present.

(a) Ferric nitrate was used to make up standards both with nitric and hydrochloric acid solutions of thoronol. In both acids it was found that Beer's Law held only for the more dilute iron solutions. At higher acidity and high ferric concentrations the standard lines curved very sharply (Fig. 5). The extinction coefficient (E) of the ferric/thoronol complex obtained from the straight line portion of the standard curves (Fig. 5) fell from 325 to 57 on changing from 0.1 to 0.25 normal hydrochloric acid medium. The absorption spectrum of the complex was plotted against the thoronol blank (Fig. 6) in order to see if the ferric salt was being further complexed at higher ferric concentrations. The spectra of the two solutions in this graph are similar and both have peaks at 531 mμ indicating only one complex, yet one of these solutions has an iron concentration eight times that of the other solution and has only twice its optical density. It may be that the absorption spectra of two complexes in solution are very similar.

(b) The uranyl/thoronol complex was examined in HCl and HNO_3 media over the acidity range 0.025 to 0.5 normal (Fig. 7). Here again, Beer's Law was only obeyed at the very low acidity, the stronger acid apparently causing further complexing. The extinction coefficient for the uranyl/thoronol complex varied from 350 in 0.025 normal acid to 15 in in 0.5 normal acid. Hence, in order to minimise the interfering effects due to uranyl and ferric ions, the plutonium/thoronol complex should be measured in 0.25 normal acid. Tables X to XIV and Table XVI of the Appendix illustrate the effect of time and acidity in the optical density of the ferric/thoronol and uranyl/thoronol complexes respectively. Tables XV and XVII gave the extent of the interfering effects of ferric ion and uranyl ion in the estimation of plutonium by the thoronol method.

10. Elimination of interferences

10.1 Fluoride ion complexes plutonium and causes gross interference in the formation of the plutonium/thoronol complex. (see Table XVIII in Appendix). This interference can easily be removed by addition of aluminium nitrate and precipitation with ammonia followed by solution in dilute acid. The interfering effect due to 500 times its weight of sodium fluoride on the plutonium complex can be eliminated and by carrying out the operation in a centrifuge tube the plutonium can be estimated to within a few per cent in half an hour. A more detailed procedure and the results obtained are given in the Appendix (para. 7 and Table XIX).

10.2 As ammonium nitrate and iron salts are often met with in plutonium solutions, simulated aqueous raffinates were made up synthetically and plutonium estimated by two different solvent extraction processes.

(i) Trifluorothenoyl acetone (TTA) Extraction

The synthetic mixture was diluted with 0.1 N.HNO_3 and extracted with TTA/Benzene. The T.T.A. after a water wash was treated with 1 ON.HNO_3 to remove the plutonium which was then diluted, thoronol was added and the solution examined in the Spekker.

(ii) Tributyl phosphate (TBP) Extraction

The synthetic mixture was diluted and made 1.5 molar in aluminium nitrate and 2 N in nitric acid. The plutonium was extracted into T.B.P. then washed out of the solvent with aqueous hydroxylamine. After a benzene wash, the aqueous extract was diluted, thoronol was added and the solution examined in the Spekker.

Further details of methods (i) and (ii) are given in the Appendix, (Para. 8). Both methods have furnished results ±3% in error.

11. Discussion

11.1 The general analytical procedure which has been worked out gives good results in estimating quantities of the three different valency states of plutonium, provided the plutonium does not contain interfering cations or anions. The relative interference of a number of these ions are given in the Appendix (Tables XV, XVII and XVIII). The general procedure also requires the optical density to be measured five minutes after addition of the plutonium. The plutonium/thoronol complex is not stable for long periods particularly at the higher acidities such as 1 normal acid. Even at 0.25 normal acid, the higher concentrations of plutonium give complexes which fade gradually over an hour although the lower plutonium concentrations at this acidity give much more stable colours. However, at the lower acidities (0.05 to 0.10 normal) the plutonium/thoronol complex is much more stable for both the lower and higher plutonium concentrations. These low acidities do not cause precipitation of colloidal tetravalent plutonium at the concentrations used in these estimations. Variation of optical density with time for the various acidities and plutonium concentrations are given in the Appendix (Tables I - IX).

11.2 The separation of fluoride from tetravalent plutonium via the hydroxide precipitation of aluminium gives good results with varying quantities of fluoride originally present. (Table XIX in Appendix). When only a small quantity of fluoride is present, its interfering effect on the complex can be removed, simply by addition of an excess of aluminium. Here the aluminium need not be removed by previous precipitation, and the optical density of the complex can be measured directly on the Spekker. Time did not permit the investigation of the possibility of differentiating between fluorides of plutonium of different valency states using thoronol reagent.

11.3 The two solvent extraction processes quoted for separation from interfering impurities may give erroneous results if all the organic material is not removed. This removal could be ensured by taking the final aqueous solutions to dryness with nitric/perchloric acid mixture.

11.4 Uranyl ion plus thoronol gives a low extinction coefficient (E = 15 in 0.5 N.HCl) similar to that of the plutonyl/thoronol complex (E = 16) and in contrast to tetravalent uranium (E - 9000) or plutonium (E = 11,000). Although the tetravalent uranium complex is relatively unstable, thoronol reagent would prove useful in spotting small amounts of tetravalent uranium in uranyl compounds.

11.5 Different techniques could be employed for the estimation of plutonium in various solutions depending on the presence of other interfering materials. For example, if small amounts of uranyl and ferric salts were present, the plutonium/thoronol complex should be directly estimated in stronger acid (0.25 normal) rather than weaker acid (< 0.1 normal) owing to the considerable decrease in the extinction coefficients of those impurities at the higher acidity.

12. SUMMARY

12.1 A rapid colorimetric method has been developed for the determination of plutonium over the range 5 to 100 μg with an accuracy of ±1% at the 100 μg level. The coloured plutonium/thoronol complex which is measured on a Spekker absorptiometer can be used to estimate the amounts of the 3, 4 and 6 valent states present in a plutonium sample. The effects of a number of interfering cations have been studied, in particular iron and uranium. Anions that complex plutonium inhibit the formation of the coloured complex. Methods are suggested to remove or at least to minimise the effects due to most of the complexing cations such as iron or anions such as fluoride.

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1. Kuznetzov, V. I. J. Gen. Chem. (U.S.S.R.) 14, 914-19 (1944)

2. Thomason, P. F., Perry, M. A., and Byerly, W. M., Anal. Chem. 21 1239 (1949)

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APPENDIX

1. Effect of Time on optical density of the plutonium/thoronol complex at different acidities.

Table I

Acidity 0.05 normal HNO_3

Time (minutes)	1 microgram Pu/ml of solution Optical Density	2 μg Pu O.D.	4 μg Pu O.D.	5 μg Pu O.D.
Zero (calc.)	0.220	0.440	0.840	0.985
2 (mins.)	0.220	0.440	0.851	1.005
5 "	0.220	0.440	0.860	1.025
10 "	0.221	0.444	0.865	1.034
20 "	0.221	0.445	0.870	1.049

Table II

Acidity 0.10 N HNO_3

Time (minutes)	1 μg Pu/ml of solution Optical Density	2 μg Pu/ml O.D.	4 μg/ml O.D.	5 μg/ml O.D.
Zero (calc.)	0.213	0.433	0.845	1.020
2 (mins.)	0.213	0.433	0.846	1.030
5 "	0.213	0.433	0.847	1.040
10 "	0.213	0.433	0.847	1.043
20 "	0.213	0.434	0.849	1.049

Table III

Acidity 0.25 N HNO_3

Time (mins.)	1 µg Pu/ml Solution	2	4	5	6
Zero (calc.)	0.202	0.385	0.775	0.970	1.24
2 (mins.)	0.202	0.385	0.775	0.967	1.18
5 "	0.202	0.385	0.775	0.965	1.10
10 "	0.202	0.385	0.772	0.962	1.061
20 "	0.200	0.378	0.766	0.950	1.035

Table IV

Acidity 0.50 N HNO_3

Time (mins)	1 µg Pu/ml	2	4		6
Zero (calc.)	0.178	0.325	0.660		0.975
2 (mins.)	0.168	0.330	0.640		0.860
5 "	0.165	0.315	0.610		0.760
10 "	0.165	0.305	0.545		0.625
20 "	0.160	0.285	0.400		0.440

Table V

Acidity 1.00 N HNO_3

Time (mins.)	1.2 µg Pu/ml	2	4		6
Zero (calc.)	0.220	0.330	0.540		
2 (mins.)	0.210	0.320	0.535		
5 "	0.200	0.315	0.530		0.590
10 "	0.191	0.310	0.521		0.550
20 "	0.182	0.294	0.489		0.491

Table VI

Acidity 0.05 N HCl

Time (mins.)	1 µg	2 g	4	5 µg Pu/ml
Zero (calc.)	0.202	0.402	0.800	0.945
2 (mins)	0.202	0.402	0.802	0.964
5 "	0.202	0.402	0.805	0.982
10 "	0.202	0.402	0.808	0.993

Table VII

Acidity 0.10 N HCl

Time	1 µg	2	4	5
0	0.192	0.393	0.792	0.983
2	0.191	0.394	0.795	0.989
5	0.190	0.395	0.798	0.995
10	0.189	0.396	0.804	1.004

Table VIII

Acidity 0.25 N HCl

Time	1 µg	2	4	5	6
0	0.184	0.358	0.731	0.900	1.072
2	0.183	0.357	0.732	0.900	1.072
5	0.182	0.356	0.733	0.900	1.070
10	0.181	0.354	0.726	0.891	1.040

Table IX

Acidity 0.50 N HCl

Time	1.2	2	4		6
0	0.218	0.328	0.575		0.794
2	0.209	0.319	0.565		0.767
5	0.200	0.310	0.555		0.740
10	0.196	0.306	0.540		0.690
20	0.189	0.303	0.510		0.610

2. The ferric/thoronol complex. Plutonium absent

A series of aliquots of 0.020 molar ferric nitrate were added to 2.5 mls. of 0.1% thoronol in water and the whole made up to 25 mls. at the appropriate acidity.

Table X

Acidity 0.01 N HCl

Time	0.2 ml	1 ml
5 (mins.)	0.55	0.83

Table XI

Acidity 0.1 N HCl

Time (mins.)	0.1 ml	0.4 ml	0.5 ml	2 mls.	5 mls.	10 mls.
2	0.105	0.409	0.498	0.602	0.655	0.722
5	0.106	0.410	0.498	0.603	0.655	0.722
10	0.106	0.410	0.499	0.604	0.655	0.723

Table XII

Acidity 0.25 N HCl

Time (mins.)	0.5 ml	1 ml	1.5 mls	2 mls	5 mls	10 mls
2	0.101	0.199	0.345	0.345	0.435	0.520
5	0.100	0.198	0.345	0.345	0.435	0.521
10	0.101	0.199	0.345	0.345	0.435	0.521

Table XIII

Acidity 0.1 N HNO_3

Time	0.5 ml	5 mls	10 mls
5 (mins.)	0.520	0.687	0.750

Table XIV

Acidity 0.25 N HNO_3

Time	0.5 ml	1.0 ml	1.5 mls	2.0 mls	5.0 mls	10.0 mls
5 (mins.)	0.202	0.364	0.408	0.446	0.512	0.583

3. Interference of ferric ion in plutonium estimation by thoronol

Table XV

Acidity 0.25 N HCl

		Optical Density
No Fe'''	2 µgs Pu per ml	0.356
11 µgs Fe'''	2 " " " "	0.365
25 µgs Fe'''	2 " " " "	0.480
No Fe'''	4 " " " "	0.730
5 µgs Fe'''	4 " " " "	0.730
11 µgs Fe'''	4 " " " "	0.730
25 µgs Fe'''	4 " " " "	0.770

4. The Uranyl/thoronol complex. Plutonium absent

A series of aliquots of 0.044 molar uranyl nitrate were added to 2.5 mls. of 0.1% thoronol reagent and the whole made up to 25 mls. at the appropriate acidity.

Table XVI

	Aliquot			These optical densities were stable over 15 to 30 minutes.			
Acidity	0.2ml	0.5ml	1.0ml	3.0mls	5.0mls	8.0mls	10.0mls
0.025 N HCl	0.682	0.975	-	-	-	-	-
0.10 N HCl	-	-	0.750	1.00	1.265	-	-
0.25 N HCl	-	-	0.286	0.633	0.840	-	1.109
0.50 N HCl	-	-	0.150	0.341	0.523	0.705	0.840
0.035 N HNO_3	0.732	-	-	-	-	-	-
0.10 N HNO_3	-	-	0.822	1.150	-	-	-
0.25 N HNO_3	-	-	0.415	0.750	0.970	-	1.135
0.50 N HNO_3	-	-	0.260	0.490	0.621	-	-

5. Interference or uranyl ion in plutonium estimation by thoronol

Table XVII

Acidity 0.25 N HCl

		Optical Density
No uranium	2 µgs Pu per ml	0.356
20 µgs U per ml	2 µgs Pu per ml	0.356
40 µgs U per ml	2 µgs Pu per ml	0.360

6. Interferences of Various Anions

25 mls. of 0.25 N HCl containing 2 µgs Pu/ml plus microgram quantities of the various salts listed. Where the anions do not interfere the Spekker reading would be 0.356.

Table XVIII

	Quantity of salt added	Spekker Reading (5 minutes)
K Oxalate	1,700 micrograms	0.040
	170 "	0.250
	17 "	0.350
NH_4NO_3	160,000 "	0.050
	80,000 "	0.070
	4,000 "	0.355
Na_2HPO_4	14,000 "	0.130
	1,400 "	0.241
	140 "	0.269
	14 "	0.350
Na_2SO_4	140,000 "	0.021
	14,000 "	0.323
	1,400 "	0.355
$K_2Cr_2O_7$	250,000 "	0.250
	25,000 "	0.356
NaF	4,200 "	0.110
	420	0.258
	42 "	0.342

7. Elimination of Interferences due to Fluoride

After addition of aluminium nitrate to the plutonium solution containing the fluoride in a 15 ml centrifuge tube, ammonium hydroxide is added to precipitate the aluminium and plutonium. The mixture is then centrifuged and the supernatant liquid removed. The precipitate is dissolved in dilute hydrochloric acid; here, warming is not usually necessary. This precipitation is repeated twice and the final acid solution is treated with hydroxylamine and then sodium nitrite. The solution is then made up to the required acidity, thoronol added and the plutonium estimated. The result is usually only a few per cent low. Some typical results are given in the table below.

Table XIX

NaF	Al	Pu present	Pu found
8 mgs	4 mgs	25 µg	24 µg.
4	4	50	49.5
8	4	50	49
10	5	100	99

8. Elimination of Interferences by Solvent Extraction

(i) T.T.A. Extraction

Synthetic mixtures were made up containing iron, uranium, plutonium and ammonium salts to simulate aqueous raffinate from the Plutonium Extraction Process. Ten mls. of such a mixture is diluted to 100 mls. with 0.1 N HNO_3 and extracted in two lots with 50 mls. (2 x 25 mls.) of T.T.A. (0.25 molar in benzene). This T.T.A. solution was washed with 50 mls. water then with 3 x 5 ml. lots of 10 N HNO_3. An aliquot of this nitric acid solution (0.5 ml.) is diluted to 25 mls. with water and thoronol reagent and the plutonium estimated.

(ii) T.B.P. Extraction

Half a ml. of the synthetic mixture above is made up to 10 mls. of solution 1.5 molar in aluminium nitrate and 2 molar in nitric acid. This is extracted with 3 x 5 ml. lots of conditioned T.B.P. solution with 2 x 10 ml. lots of 0.05 molar by hydroxylamine, and this aqueous extract washed with benzene. After addition of slight excess of sodium nitrite, the solution is made up to 25 mls. with water and the plutonium estimated. In a series of experiments using both these extraction methods the results varied between plus and minus 3%.

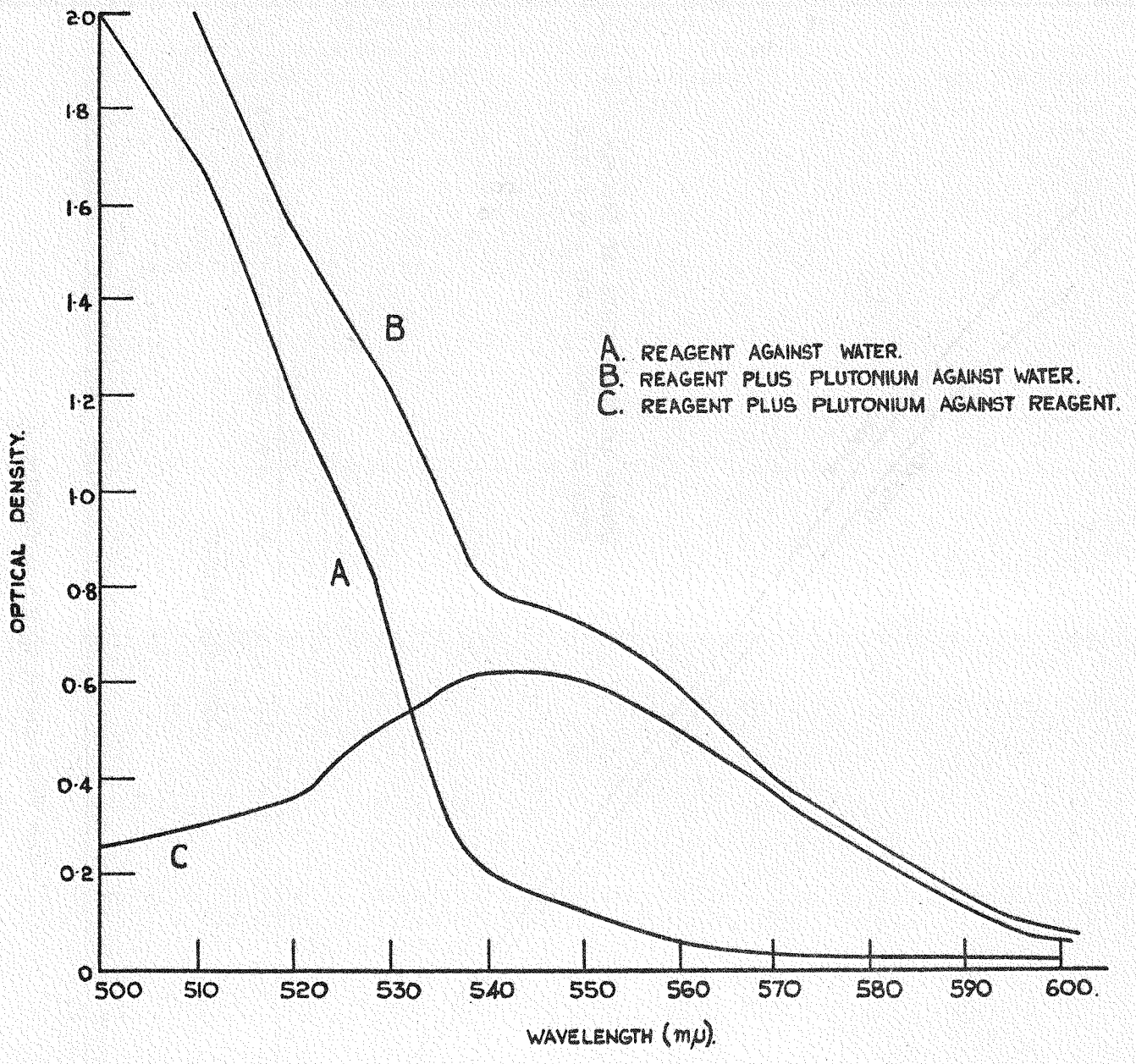


FIG. 1. ABSORPTION SPECTRUM OF PLUTONIUM / THORONOL COMPLEX.

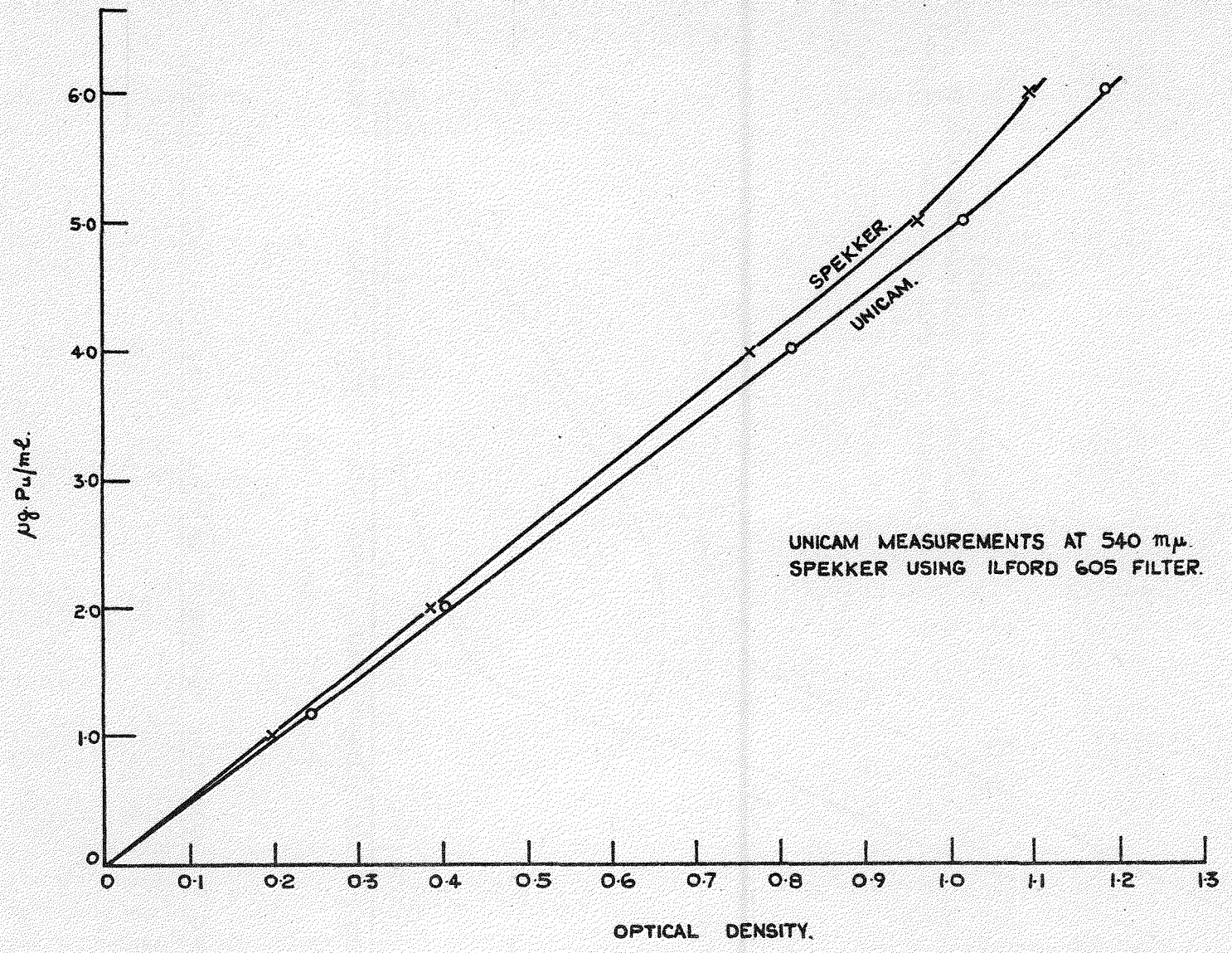


FIG. 2. RELATIVE SENSITIVITY OF SPECTROPHOTOMETER & ABSORPTIOMETER. COMPARISON OF UNICAM & SPEKKER.

4 cm PATH LENGTH, ACIDITY 0·25N HNO_3.

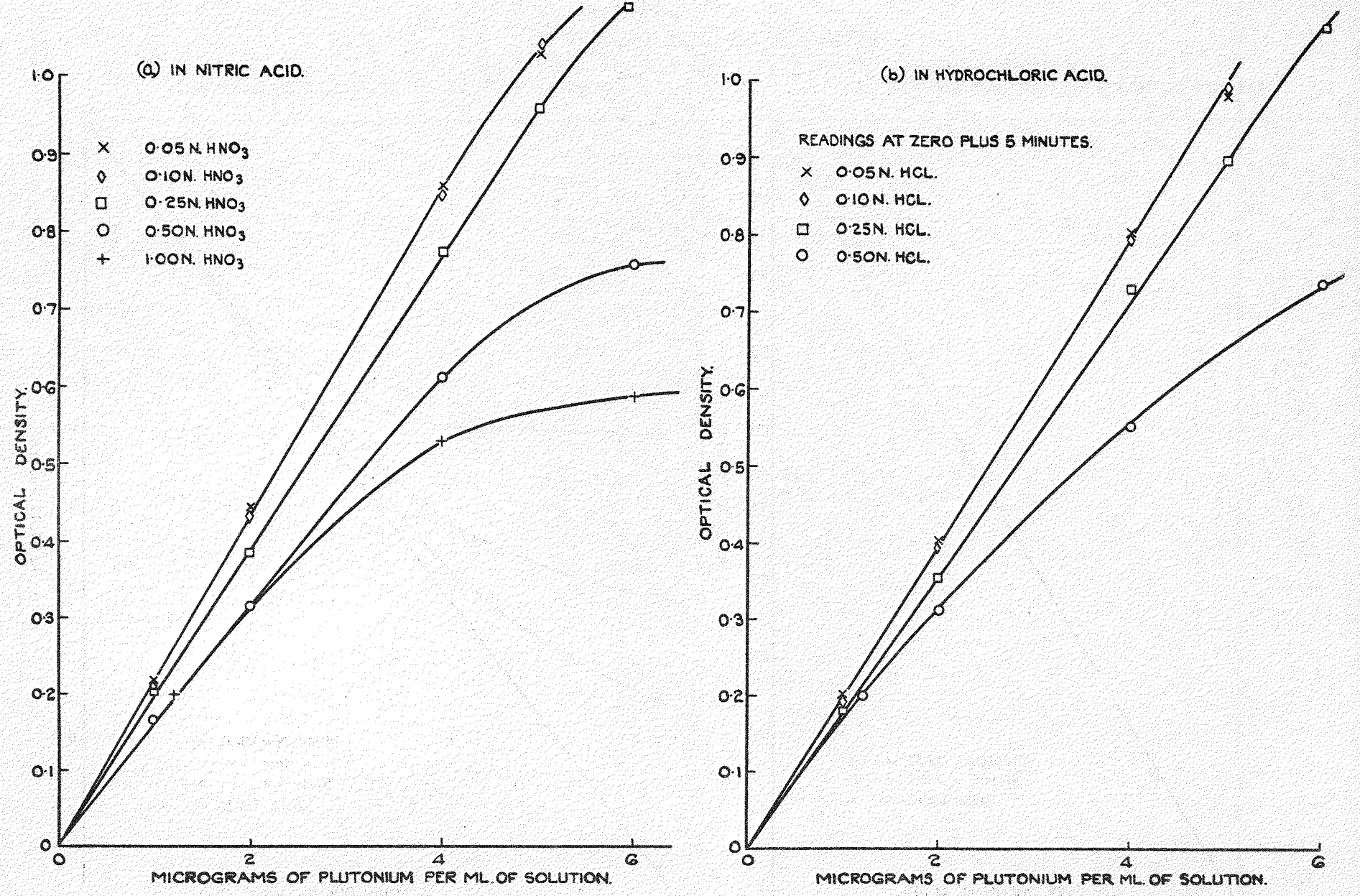
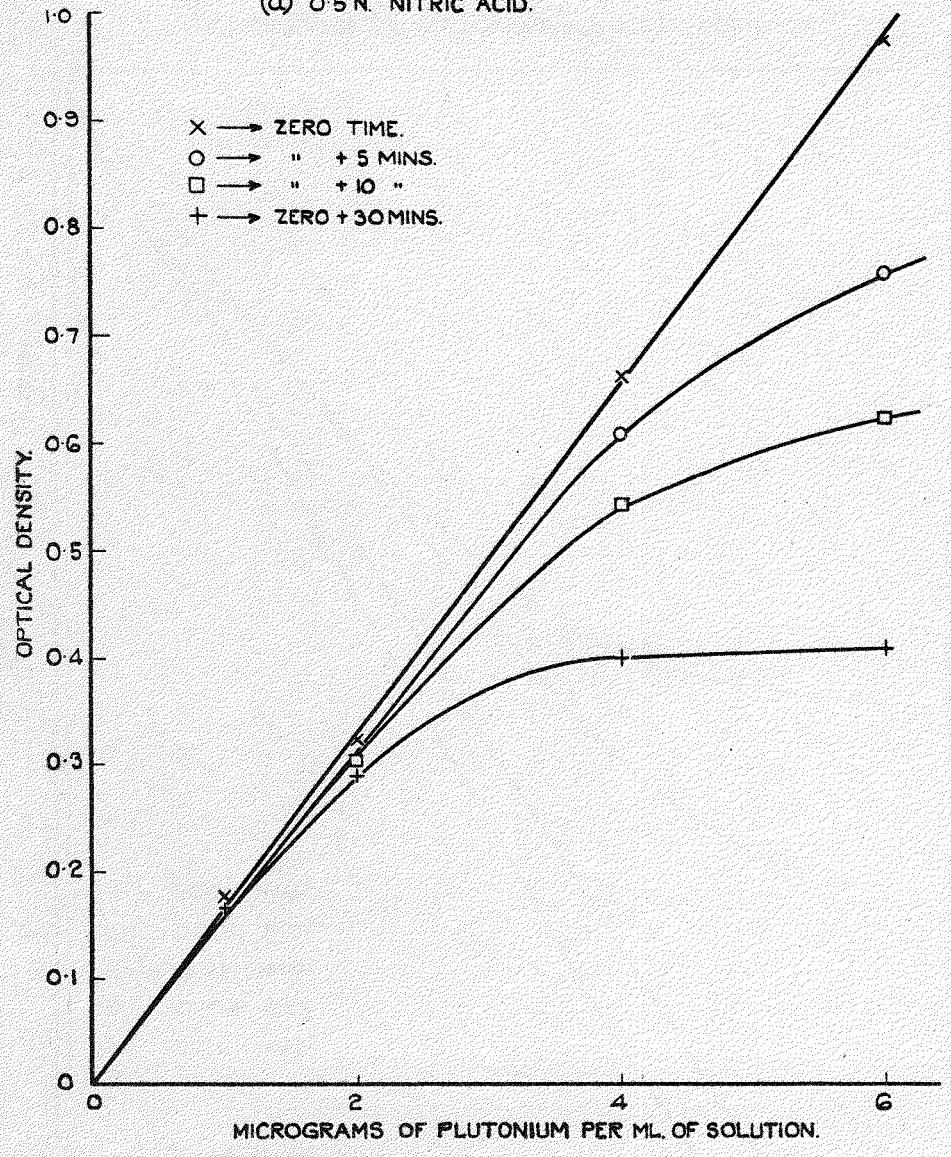


FIG. 3. EFFECT OF ACIDITY ON COMPLEX.



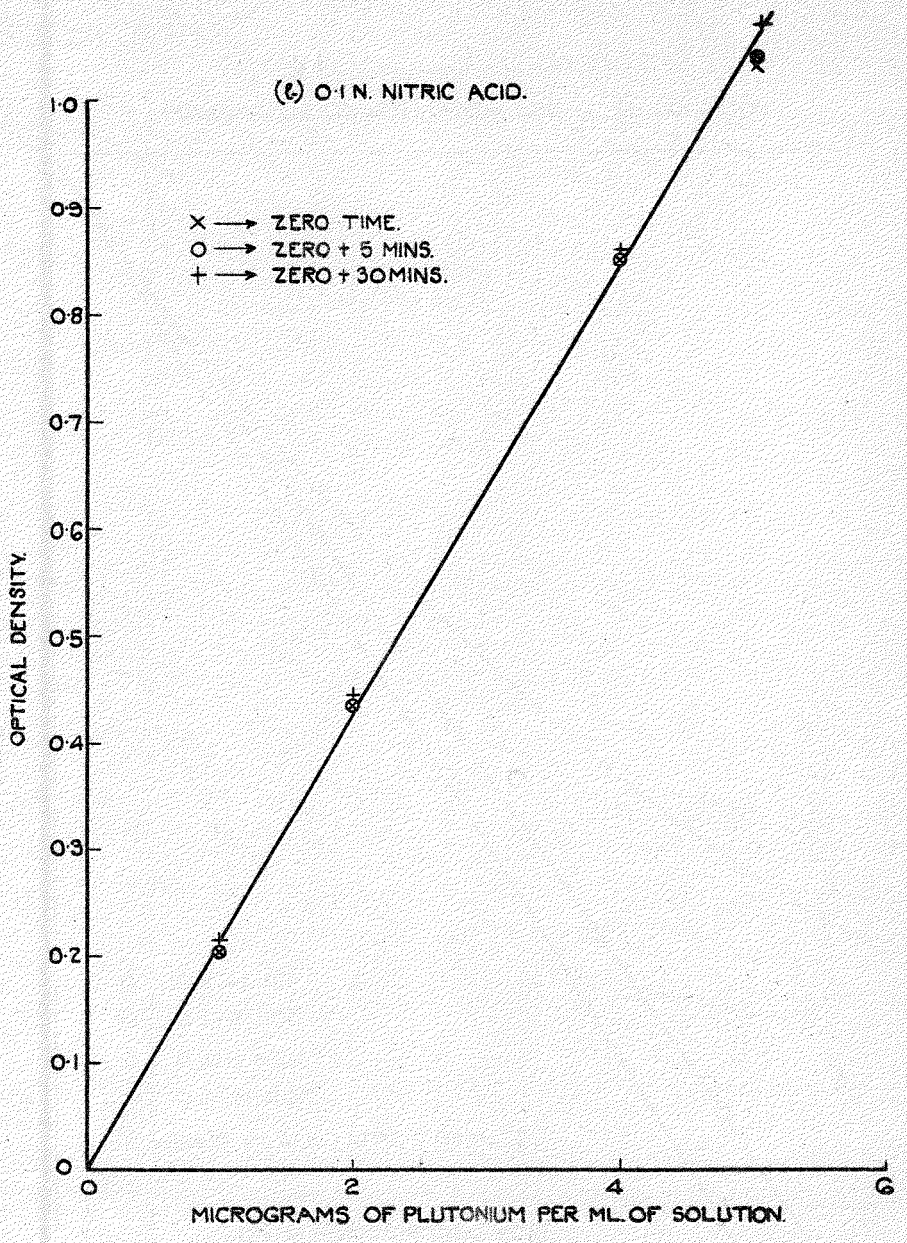


FIG. 4. EFFECT OF TIME ON COMPLEX.

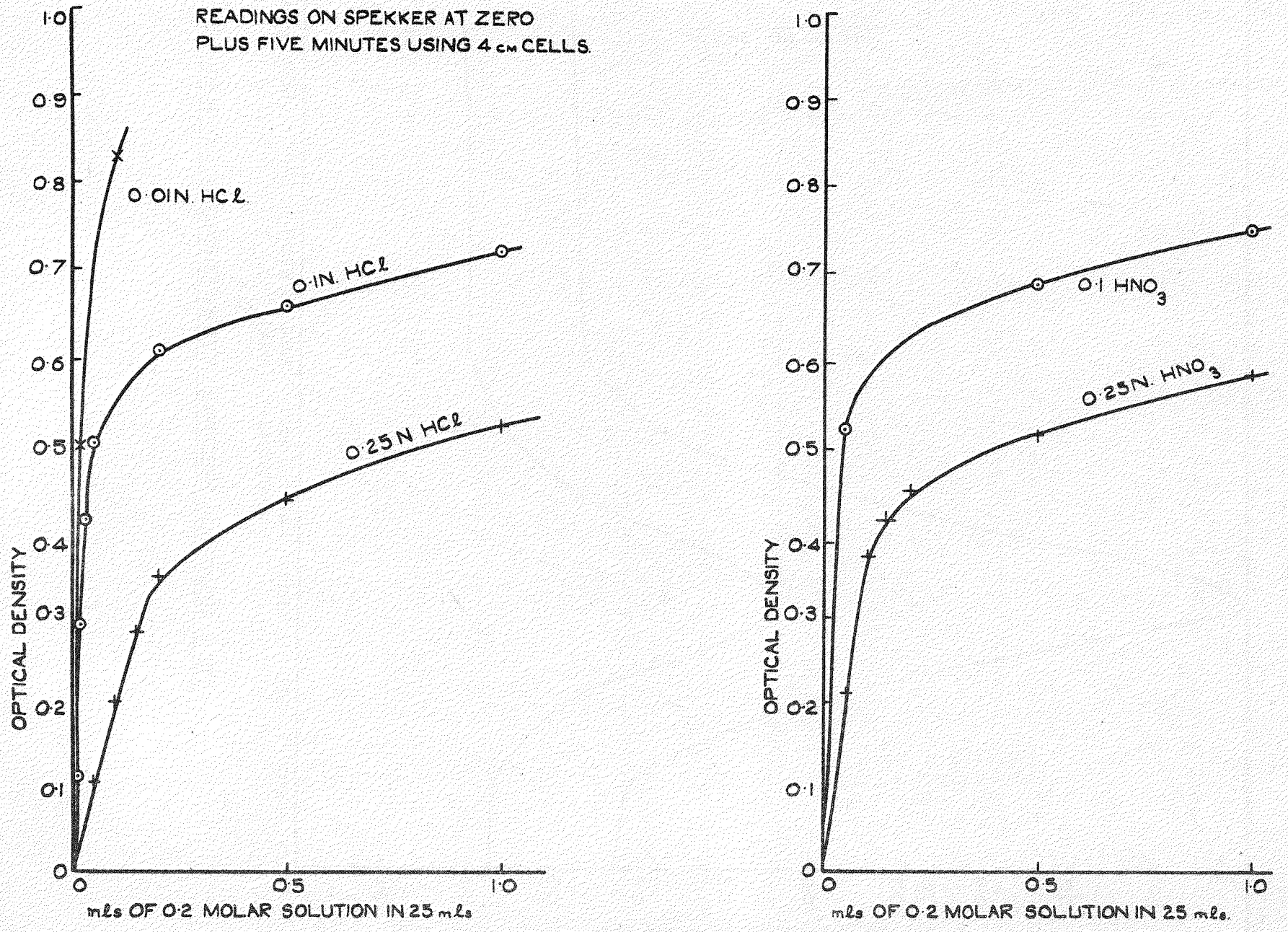


FIG. 5. EFFECT OF ACIDITY ON FERRIC/THORONOL COMPLEX.

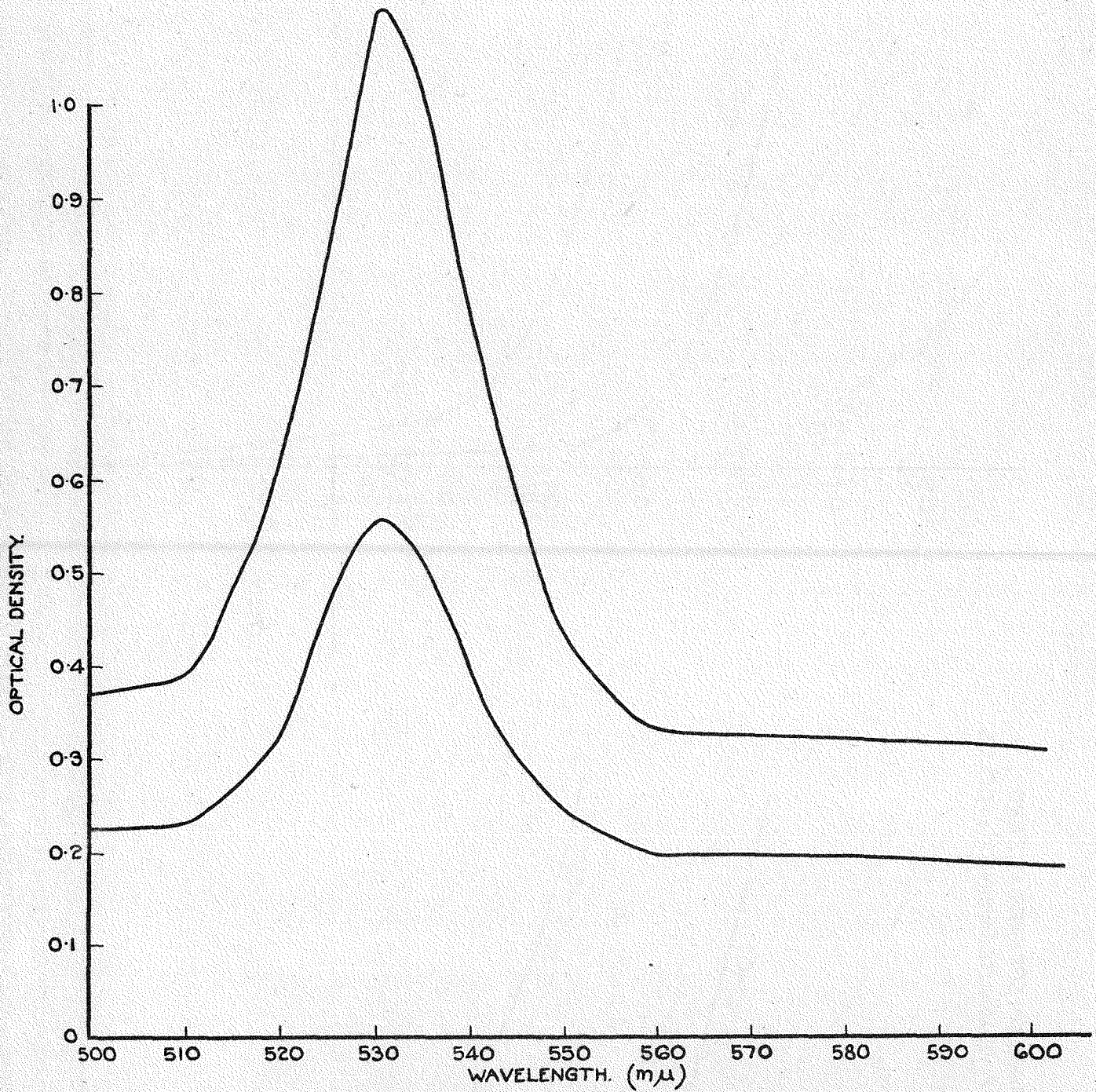


FIG. 6. ABSORPTION SPECTRUM OF FERRIC/THORONOL COMPLEX.

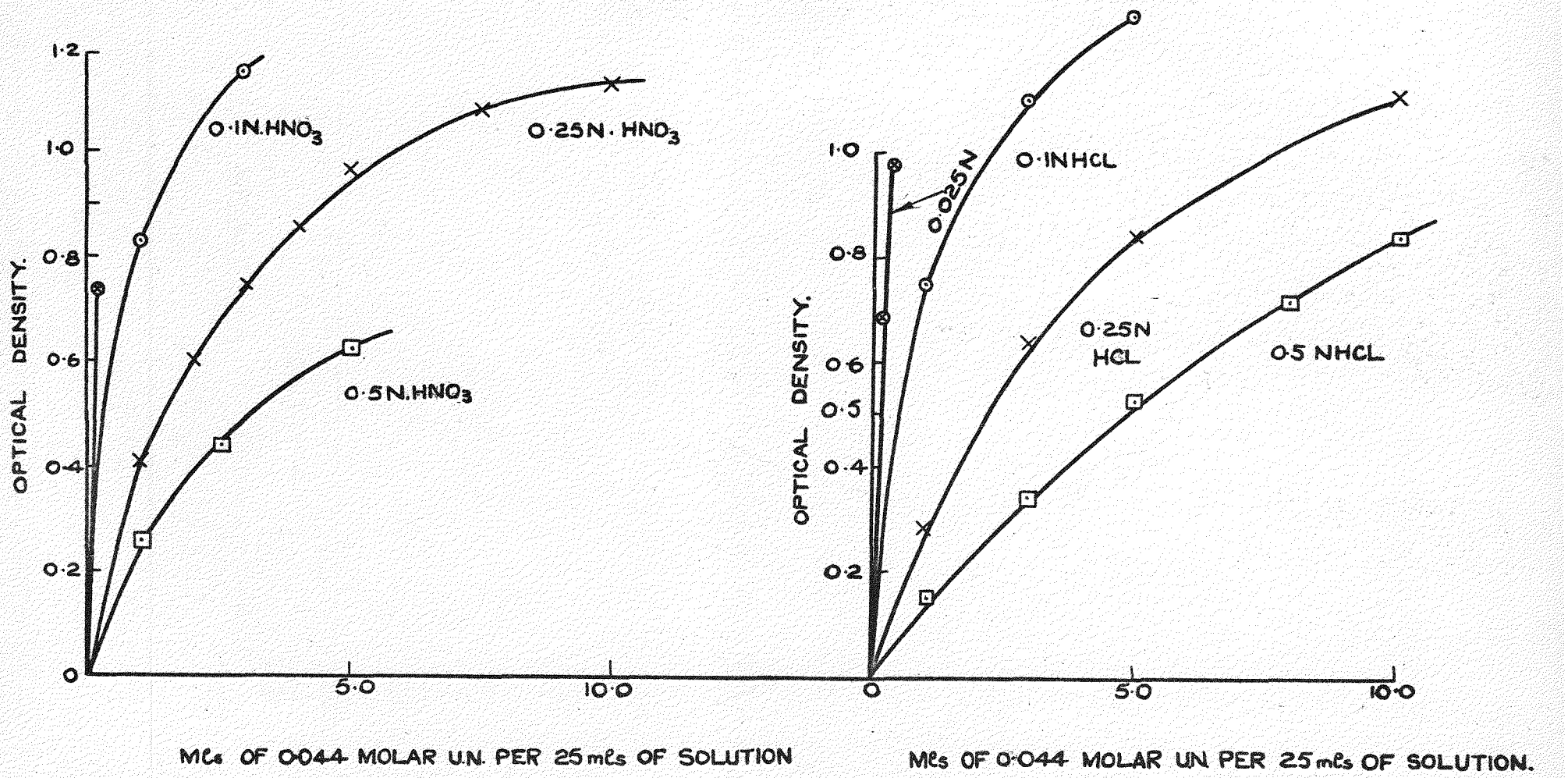


FIG. 7. EFFECT OF ACIDITY ON URANYL / THORONOL COMPLEX.

SPEKKER READINGS AT ZERO PLUS FIVE MINUTES

USING 4 CM CELLS.