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THE DETERMINATION OF FREE ACID IN PLUTONIUM SOLUTIONS

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ABSTRACT

A method is described for the determination of free acid in plutonium solutions having an excess acidity greater than 0.2 normal. The hydrolytic interference of plutonium(IV) is prevented by precipitation with potassium iodate and subsequent removal by filtration. The filtrate is then titrated with a standard base using a potentiometric end point. If plutonium(VI) is known to be absent, phenolpthalein may be used as an indicator. The standard deviation for 49 determinations was 0.9 percent.

A method is suggested for determining the amount of plutonium(VI) in a solution by the potentiometric titration of the iodate filtrate with a standard base.

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INTRODUCTION

The problem of the determination of free acid in the presence of hydrolyzable ions has long been recognized. In most cases hydrolytic interference has been prevented by the addition of complexing or precipitating agents. Recent investigators have reported methods for specific cases. Blaedel and Panos(1) determined the free acid in aluminum nitrate solution by complexing the hydrolyzable aluminum ions with oxalate prior to titrating the free acid with standard base. Pepkowitz et al.(6) used fluoride ion to suppress the hydrolysis of both aluminum and iron before titrating the free acid conductiometrically. Carson(2) tried several methods in an attempt to develop a single universal microtitration for acid in uranyl nitrate solution. These included precipitation with oxalate, complexing with fluoride, and a conversion method in which the uranium is reacted with phosphate and a correction made for the acid released.

Plutonium solutions present a complicated situation in that they may contain more than one oxidation state. Kraus and Dam,(3,4,5) in their work on the hydrolytic behavior of the various oxidation states of plutonium, showed that the hydrolysis of plutonium(III), (V), and (VI) did not interfere with the direct potentiometric titration of the free acid, the acid end point occurring before the plutonium began to precipitate. Potentiometric titration of plutonium(VI) solutions produced a curve with two inflection points, the mid-point of the first being the end point of the free acid titration. The buffering region between the two inflection points was evidently due to the formation of a soluble hydroxyl-plutonium compound.

The hydrolytic interference of plutonium(IV) is evident on titrating such a solution with standard base because of the precipitation of plutonium before the acid end point is reached. The hydrolysis produces an increase in the free acid as expressed by the general equation

$$Pu^{+4} + nH_2O \longrightarrow Pu(OH)_n^{+(4-n)} + nH^+$$

It is necessary, then, to prevent this hydrolysis if the free acid in a solution containing plutonium(IV) is to be determined. Plutonium(IV) solutions are frequently encountered in the laboratory since this oxidation state is quite stable and often results from air oxidation or disproportionation.

In an unpublished work, C. W. Bjorkland has described attempts to use the method of Blaedel and Panos(1) for determining the free acid in a solution containing plutonium(IV) ions. Only partial success was achieved because of the formation of a precipitate near the end point which would not dissolve in acid, thus preventing him from obtaining a satisfactory titration blank.

In the work described here a method was developed, and used successfully, to determine the free acid in solutions containing plutonium in one or more of its oxidation states. It is based on the removal of plutonium(IV) from solution by precipitation as the iodate and subsequent potentiometric titration of the filtrate with a standard base. The results reported by Kraus and Dam regarding the noninterference of plutonium(VI) were confirmed.

RECOMMENDED METHOD

CAUTION

Any work involving the handling of plutonium-containing materials should be done under approved conditions and in laboratories designed for the adequate protection of the worker. Rules recommended by the Health Group for the safe handling of such materials should be rigidly followed.

Apparatus

1. pH Meter, Beckman, Model H-2, equipped with a glass-saturated calomel electrode system.
2. Flask, conical, 200-ml. narrow mouth and 250-ml. wide mouth.
3. Funnel, Buchner type, with fritted glass disc of medium porosity, 3-cm. diameter. (Insert a 2-hole rubber stopper to fit wide mouth flask; insert right angle tube for suction.)
4. Microburet, 10-ml. volume, graduated in 0.05 ml.
5. Pipets, volumetric, 50-ml. and 25-ml. (If pipets used for measuring aliquots are 1 ml. or less, it is advisable to coat them with "Desicote.")

Reagents

1. A 0.3 M potassium iodate solution, made by dissolving 128.4 grams of KIO_3 in 2 liters of distilled water and adjusting the pH to 4.3 with dilute nitric acid. (The acid end point of filtrates containing plutonium(VI) occurs at about pH 4.6.)
2. Standard sodium hydroxide (approximately 0.4 to 0.5 M). All other reagents should be of analytical reagent grade.

Procedure

The following procedure should be used only with plutonium solutions that are relatively stable in respect to existing plutonium oxidation states and do not contain citrate, tartrate, or similar buffering ions present in an anion-plutonium mole ratio greater than 5.

1. Add, with stirring, an aliquot of the plutonium solution containing up to 50 mg. of plutonium to 50 ml. of 0.3 M potassium iodate solution in a 200-ml. conical flask.

2. Filter the resulting suspension, using suction through a Buchner funnel with a medium porosity fritted glass disc, into a wide mouth conical flask. (Centrifuging rather than filtering is recommended if an adequate centrifuge installed in a satisfactory enclosure is available.)

3. Wash the precipitate with two 25-ml. portions of 0.3 M potassium iodate, collecting the washings in the original filtrate.

4. Dissolve the precipitate by pouring a few milliliters of 1 M sodium citrate onto the fritted glass disc. (If this is allowed to stand during the rest of the procedure, the plutonium iodate precipitate will dissolve and the fritted glass disc may be cleaned easily with several washings of water.)

5. Place a magnetic stirring-bar in the flask containing the filtrate and lower the glass-saturated calomel electrode system into the solution. (If the original solution is known not to contain any plutonium(VI), an indicator such as phenolphthalein may be used in place of a pH meter.)

6. Titrate with standard sodium hydroxide while stirring the solution.

7. Plot the titration curve (pH versus ml. of base) and determine the end point of the titration (mid-point of the inflection). If plutonium(VI) is present, as will be shown by two inflection points on the titration curve, take as the end point the mid-point of the first inflection.

8. Titrate 100 ml. of the 0.3 M potassium iodate solution in order to determine a blank for the titration.

9. Calculate the free-acid concentration from the normality and actual amount of the standard base used.

EXPERIMENTAL

The recommended Procedure described above was developed as a result of the following investigations.

Rather than attempting to prepare plutonium solutions of definitely known excess acidity, varying known amounts of acid were added to the iodate filtrates of plutonium stock solutions to simulate solutions of higher acidity. After the titration, the acid content of the stock solution was calculated in order to check the reproducibility of the procedure.

Plutonium(III) solutions were prepared by dissolving pure metal in either concentrated hydrochloric acid or 70 percent perchloric acid and diluting to the desired concentration.

The plutonium(IV) solution used (approximately 42 grams of plutonium per liter) contained both sulfuric and nitric acid, and on titration gave no evidence of containing any plutonium(VI). The plutonium(IV) perchlorate solution was prepared by dissolving the pure metal in 70 percent perchloric acid and bubbling ozone gas through the solution for approximately 30 minutes. After the solution had come to equilibrium, titrations gave no indication of the presence of plutonium(VI).

Plutonium(VI) nitrate solutions were prepared by treating freshly precipitated plutonium hydroxide with concentrated nitric acid and heating the resulting solution to produce some plutonium(VI) by nitrate oxidation. The plutonium(VI) perchlorate solution was prepared by dissolving the pure metal in 70 percent perchloric acid and bubbling ozone gas through the solution for several hours. This time was sufficient to produce some plutonium(VI) which was evident on titration with standard base.

In most cases samples were taken from the iodate filtrate after the titration and submitted to the radio assay laboratory, which determined the plutonium content by radiochemical analysis. The reason for this was to determine if the amount of plutonium left in the filtrate was large enough to interfere with the acid titration. The only appreciable amount of plutonium found in the filtrates was from samples containing plutonium(VI) which did not interfere in the determination of the free acid.

The titrations were carried out using a direct-reading pH meter with a glass-saturated calomel electrode system. A 10-milliliter microburet was used to add the standard base, and titration curves were constructed by plotting the pH values measured versus the milliliters of base added.

RESULTS

Plutonium(III) Solutions

Figures 1 and 2 are typical of the potentiometric titration data obtained on the filtrates from plutonium iodate precipitations from hydrochloric and perchloric acid solutions containing plutonium(III). One-milliliter aliquots of plutonium stock solution were used.

Free-acid data, of the same solutions containing varying amounts of added acid, are shown in Tables I and II. It appears that the small amount of plutonium remaining in the filtrate did not affect the titration.

Plutonium(IV) Solutions

Figure 3 shows typical potentiometric titration data obtained on the filtrates after iodate precipitation of the plutonium(IV) from solutions containing excess nitric and sulfuric acids. The data in Table III, obtained on aliquots of the same stock solution, indicate the reproducibility possible in such titrations.

Solutions Containing Plutonium(III) and (IV)

Although no *a priori* reason seemed to exist that might adversely affect applications to solutions simultaneously containing plutonium in the (III) and (IV) oxidation states, titration data were obtained as a double check. Typical data from such solutions are shown in Figure 4 and Table IV.

Solutions Containing Plutonium(VI) and (IV)

Kraus and Dam(5) observed a buffering action between pH 5 to 9 when solutions containing plutonium(VI) were titrated with a standard base. They concluded that the inflection at the start of the buffering region marked the end of the free-acid titration. They were also able to show that the formation of soluble plutonyl hydroxide $[PuO_2(OH)_2]$ took place in this buffering region.

This same buffering action was observed in the iodate filtrates from solutions containing plutonium(VI) (Figures 5 and 6). The presence of plutonium(VI) in the filtrate is apparently due to the solubility of plutonium(VI) iodate under the condition of the procedure. The free acid in these filtrates was obtained by taking as the free-acid end point the mid-point of the first inflection of the potentiometric titration curve. Attempts to use an indicator such as Bromcresol Green or p-sulfo-o-methoxybenzene-azo-dimethyl-α-napthylamine were unsuccessful evidently due to the oxidizing action of the plutonium(VI). Tables V and VI show free-acid data obtained on these plutonium(IV,VI) solutions.

The extent of the buffering action caused by the formation of plutonyl hydroxide is apparently proportional to the amount of plutonium(VI) present in the solution titrated. Since the plutonium(VI) is not removed by the iodate precipitation, potentiometric titration of the filtrate with a standard base and measurement of the buffering action might offer a means of determining the amount of plutonium(VI) present in the original solution.

Reproducibility

The standard deviation calculated for the 49 titrations reported is 0.9 percent for acid concentrations in the range of 0.2 to 8 normal.

Interferences

This iodate precipitation method was devised specifically for relatively pure plutonium solutions and could not in general be applied to solutions containing other hydrolyzable ions. As shown by the data presented, anions of strong acids do not interfere. Plutonium solutions containing citrate and tartrate ions present in a mole ratio (anion to plutonium) of about 15 were found to interfere. However, when the mole ratio was reduced to about 5, no appreciable interference resulted.

CONCLUSIONS

The free acid content of nitrate, chloride, sulfate, and perchlorate solutions containing plutonium(III), (IV), and (VI), or relatively stable mixtures of these oxidation states, can be determined by the method described. The standard deviation calculated for 49 determinations is 0.9 percent. In none of the filtrates from the plutonium(III) or (IV) solutions was there enough plutonium present to introduce errors greater than the normal experimental error. The plutonium found in the filtrates from the solutions containing plutonium(VI) was evidently present in the non-interfering (VI) state since no precipitation occurred on addition of the base.

The free-acid content of plutonium solutions containing citrate or tartrate ions in the anion-plutonium mole ratio of 5 or less can be determined by this procedure.

Basic titration of plutonium(VI) iodate filtrates suggests that a method for determining the amount of plutonium(VI) present in a solution could be devised by potentiometric titration, making use of the relation between the plutonium(VI) present and the amount of base used in the buffering region between the two inflection points of the potentiometric titration curve.

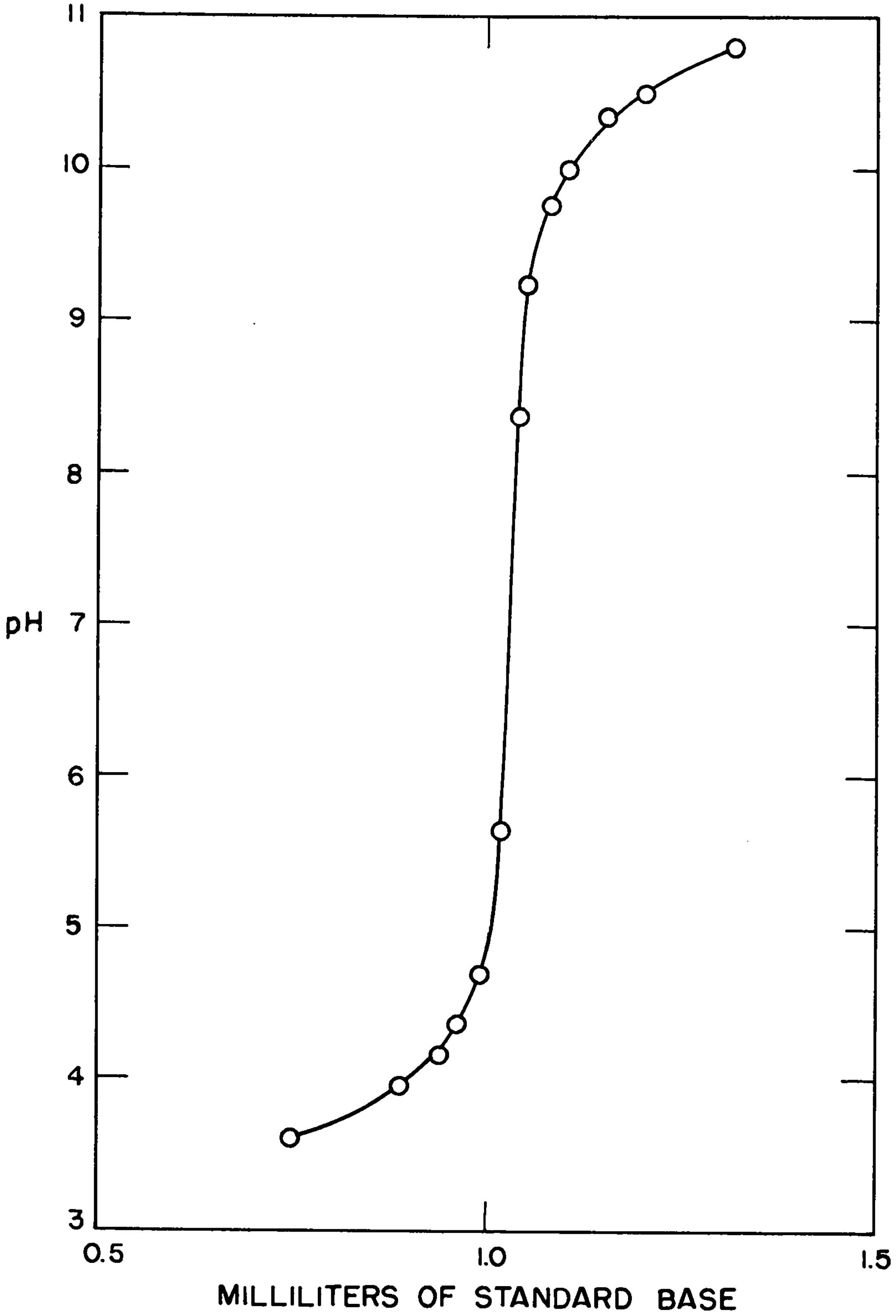

Figure 1. Potentiometric titration curve of an iodate filtrate from a plutonium(III) chloride solution.

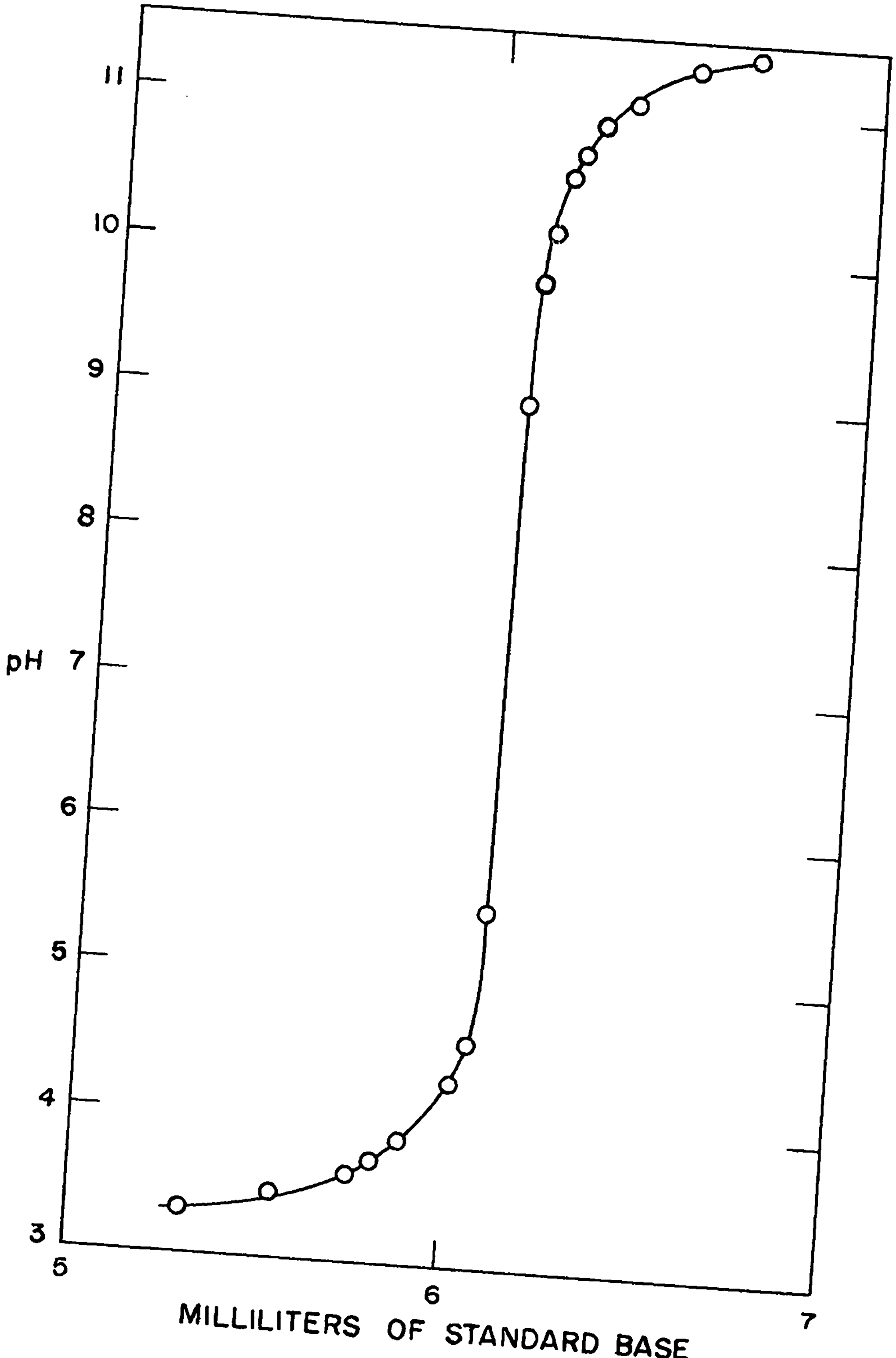

Figure 2. Potentiometric titration curve of an iodate filtrate from a plutonium(III) perchlorate solution.

Table I

DETERMINATION OF FREE ACID IN PLUTONIUM(III) CHLORIDE SOLUTIONS

Amount of Pu in Sample (mg.)	HCl Added (meq.)	Total (H^+) Found (meq.)	Free Acid Normality	Calculated (H^+) in Pu stock soln. Normality	Pu in Filtrate (mg.)
42.66	0.098	0.229	0.229	0.131	0.031
42.66	0.098	0.229	0.229	0.131	0.020
42.66	0.295	0.427	0.427	0.132	0.022
42.66	0.295	0.427	0.427	0.132	0.017
42.66	0.491	0.624	0.624	0.133	0.021
42.66	0.491	0.624	0.624	0.133	0.024
42.66	0.785	0.919	0.919	0.134	0.023
42.66	0.785	0.918	0.918	0.133	

Table II

DETERMINATION OF FREE ACID IN PLUTONIUM(III) PERCHLORATE SOLUTIONS

Amount of Pu in Sample (mg.)	$HClO_4$ Added (meq.)	Total (H^+) Found (meq.)	Free Acid Normality	Calculated (H^+) in Pu stock soln. Normality	Pu in Filtrate (mg.)
48.62	0.000	0.985	0.985	0.985	0.023
48.62	0.000	0.985	0.985	0.985	0.037
48.62	2.058	3.041	3.041	0.983	0.024
48.62	2.058	3.046	3.046	0.988	0.022
48.62	4.116	5.101	5.101	0.985	0.017
48.62	4.116	5.121	5.121	1.005	0.030

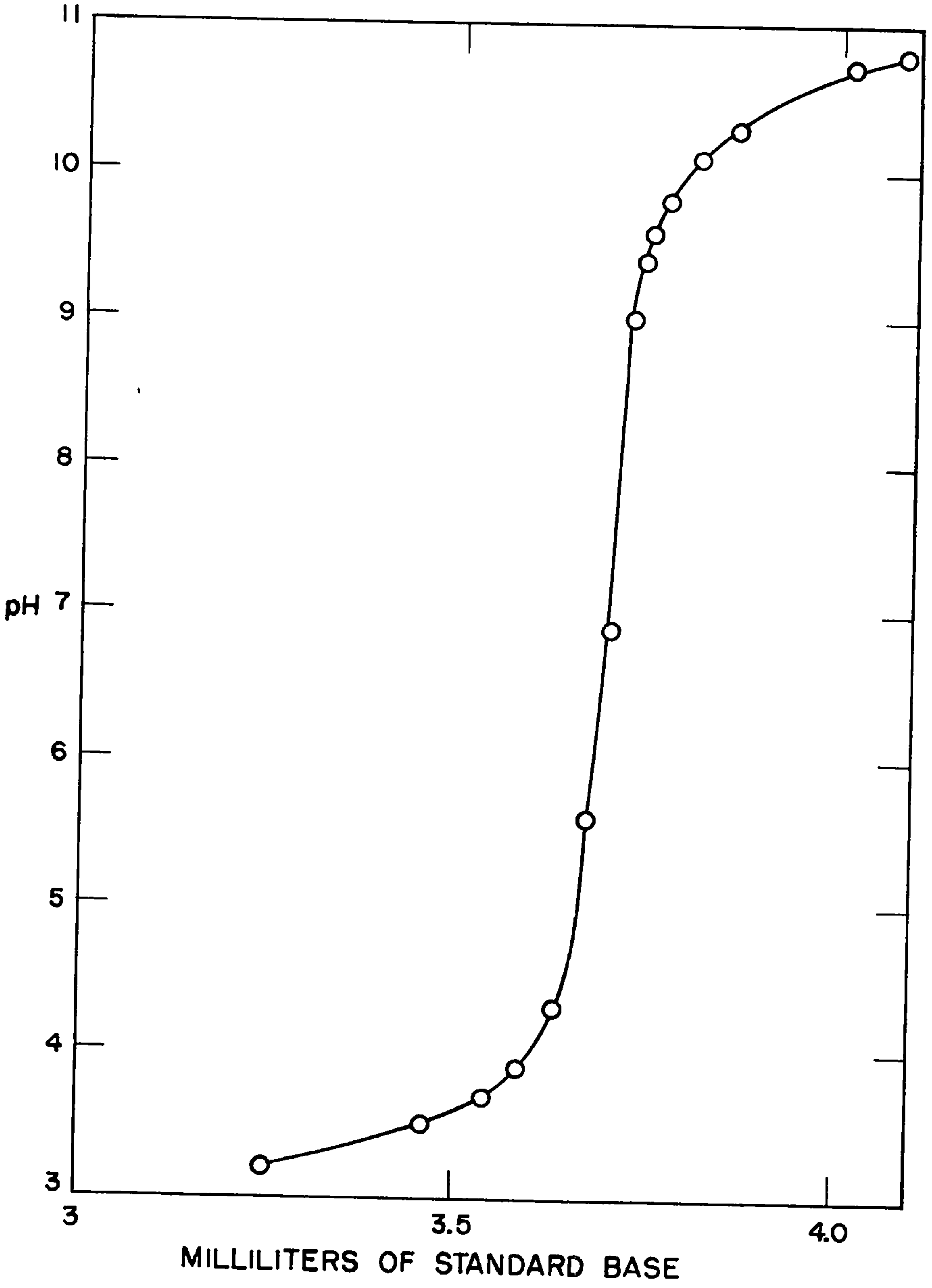

Figure 3. Potentiometric titration curve of an iodate filtrate from a plutonium(IV) nitrate-sulfate solution.

Table III

DETERMINATION OF FREE ACID IN PLUTONIUM(IV) NITRATE-SULFATE SOLUTIONS

Amount of Pu in Sample (mg.)	HNO_3 Added (meq.)	Total (H^+) Found (meq.)	Free Acid Normality	Calculated (H^+) in Pu stock soln. Normality	Pu in Filtrate (mg.)
42.12	0.000	0.608	3.040	3.040	0.082
42.12	0.000	0.621	3.105	3.105	0.097
42.12	0.116	0.725	3.625	3.045	0.094
42.12	0.116	0.729	3.625	3.065	0.165
42.12	0.347	0.958	4.790	3.055	0.074
42.12	0.347	0.958	4.790	3.055	0.076
42.12	0.578	1.187	5.935	3.045	0.076
42.12	0.578	1.183	5.915	3.025	0.081
42.12	0.924	1.533	7.665	3.045	0.077
42.12	0.924	1.541	7.705	3.085	0.056
42.12	1.155	1.758	8.790	3.015	0.090
42.12	1.155	1.762	8.810	3.035	0.099

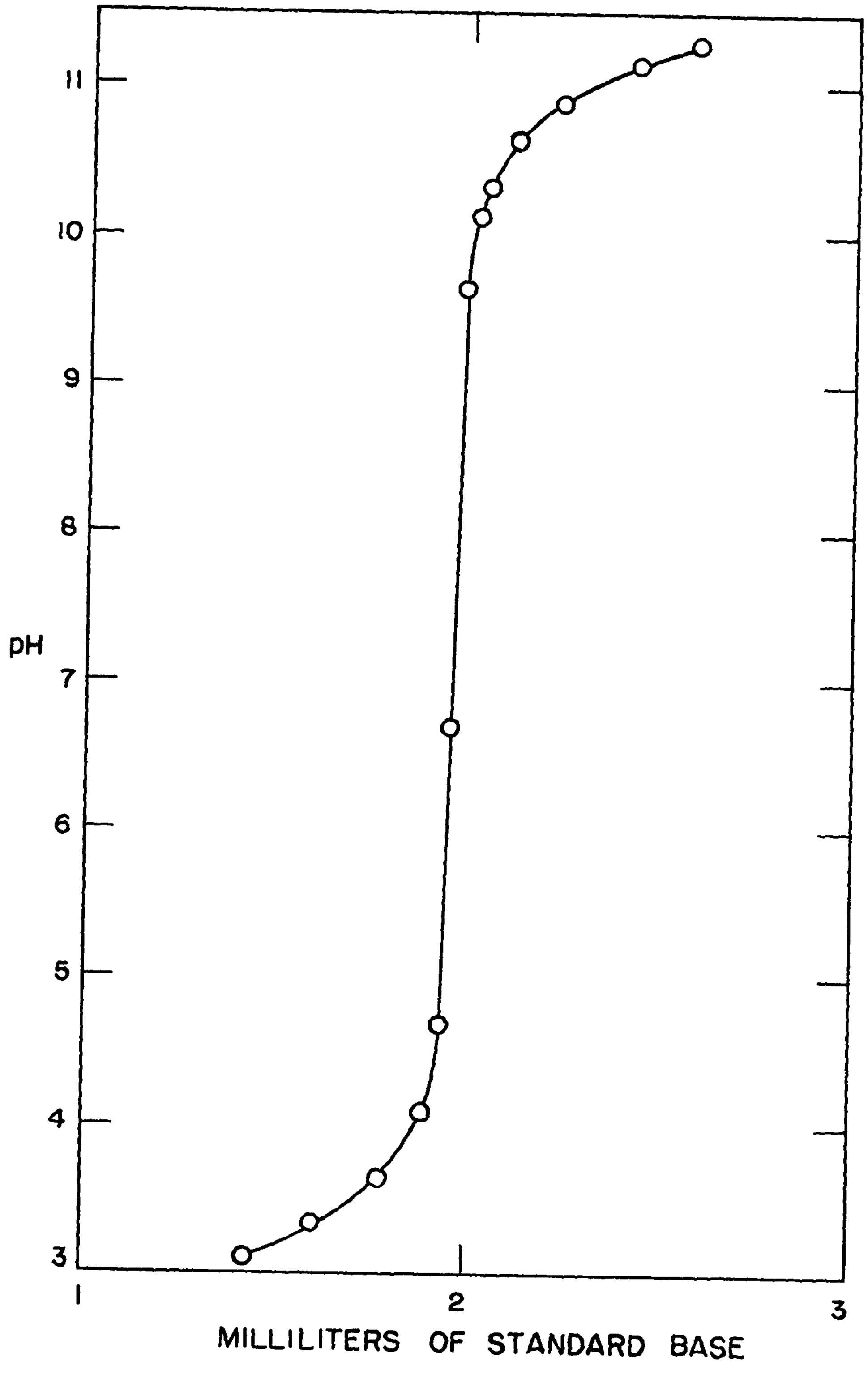

Figure 4. Potentiometric titration curve of an iodate filtrate from a perchlorate solution containing plutonium(III) and (IV).

Table IV

DETERMINATION OF FREE ACID IN PERCHLORATE SOLUTIONS CONTAINING PLUTONIUM(III) and (IV)

Amount of Pu in Sample (mg.)	$HClO_4$ Added (meq.)	Total (H^+) Found (meq.)	Free Acid Normality	Calculated (H^+) in Pu stock soln. Normality	Pu in Filtrate (mg.)
45.05	0.000	0.970	0.970	0.970	0.023
45.05	0.000	0.964	0.964	0.964	0.013
45.05	2.058	3.050	3.050	0.992	0.018
45.05	2.058	3.041	3.041	0.983	0.009
45.05	4.116	5.101	5.101	0.985	0.020
45.05	4.116	5.111	5.111	0.995	0.021

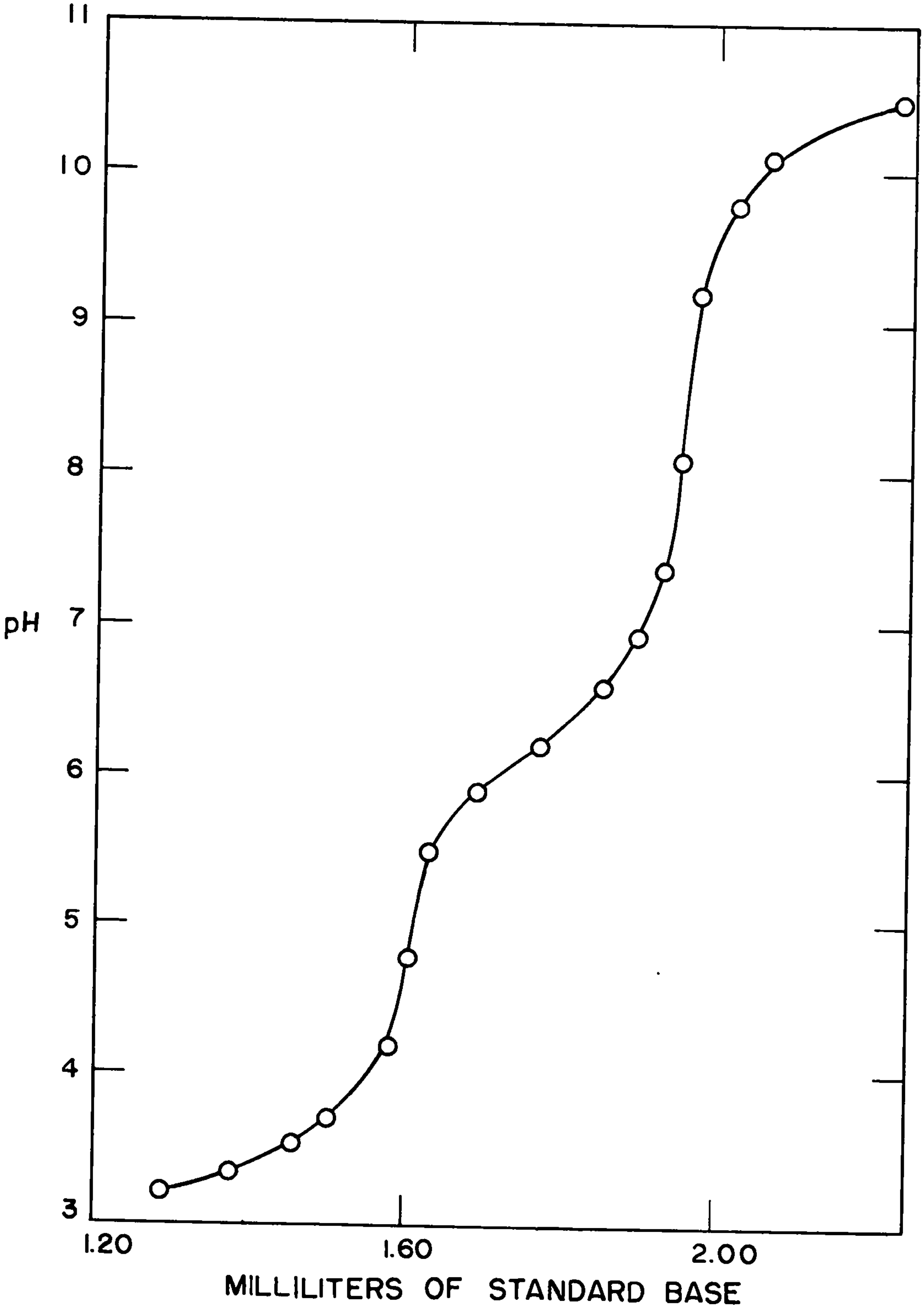

Figure 5. Potentiometric titration curve of iodate filtrate from nitrate solution containing plutonium(VI) and (IV).

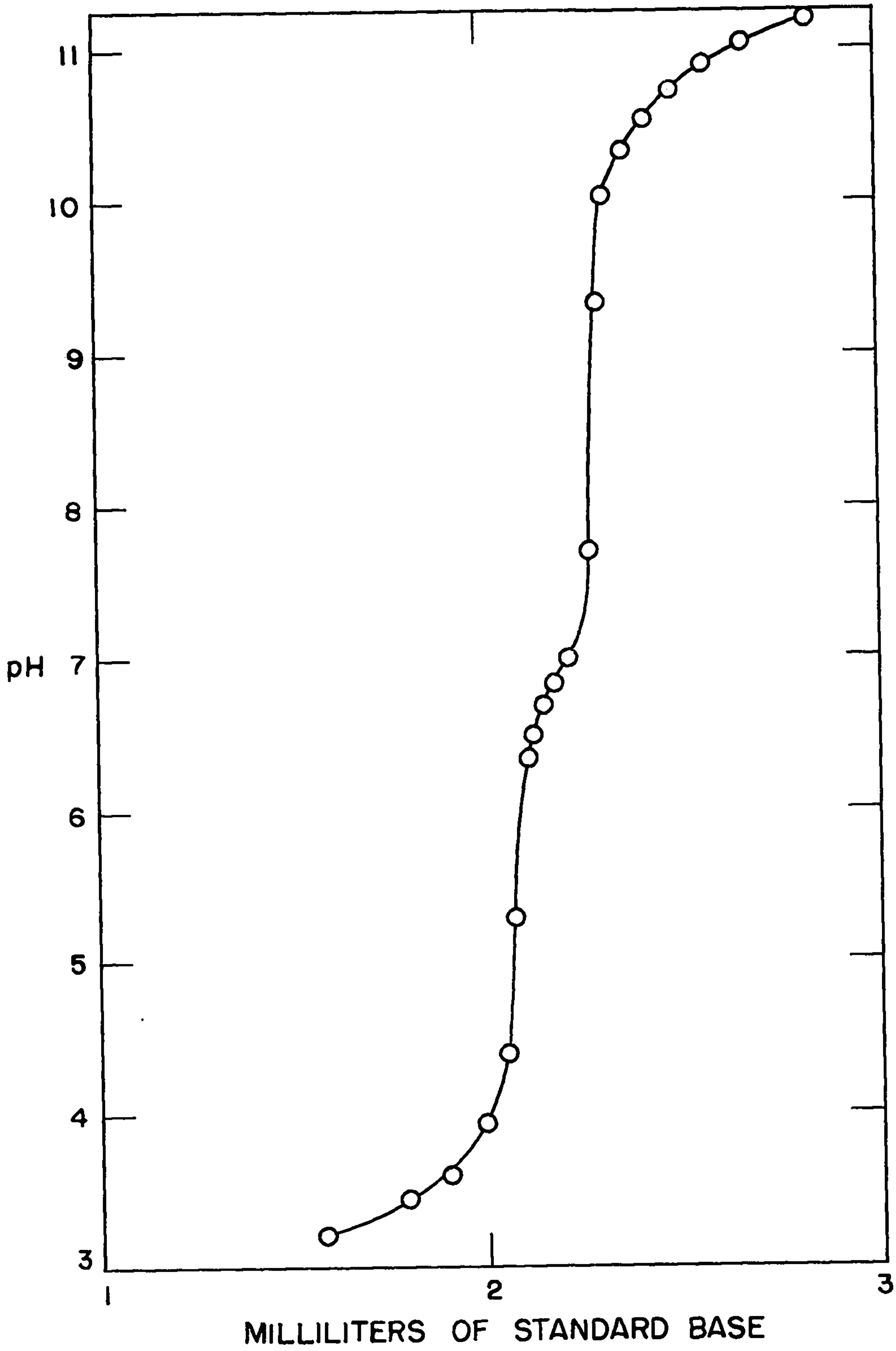

Figure 6. Potentiometric titration curve of an iodate filtrate from a perchlorate solution containing plutonium(IV) and (VI).

Table V

DETERMINATION OF FREE ACID IN NITRATE SOLUTIONS CONTAINING PLUTONIUM(IV) AND (VI)

Amount of Pu in Sample (mg.)	HNO_3 Added (meq.)	Total (H^+) Found (meq.)	Free Acid Normality	Calculated (H^+) in Pu stock soln. Normality	Pu in Filtrate (mg.)
50.54	0.000	1.406	1.406	1.406	11.7
50.54	0.000	1.412	1.412	1.412	11.8
50.54	0.347	1.758	1.758	1.411	11.6
50.54	0.347	1.771	1.771	1.424	11.5
50.54	0.578	1.991	1.991	1.413	11.8
48.43	0.000	1.389	1.389	1.389	15.1
48.43	0.000	1.381	1.381	1.381	10.1
48.43	0.580	1.976	1.976	1.396	11.2
48.43	0.580	1.942	1.942	1.362	7.6
48.43	0.927	2.321	2.321	1.394	11.1
48.43	0.927	2.330	2.330	1.403	11.6

Table VI

DETERMINATION OF FREE ACID IN PERCHLORATE SOLUTIONS CONTAINING PLUTONIUM(IV) and (VI)

Amount of Pu in Sample (mg.)	$HClO_4$ Added (meq.)	Total (H^+) Found (meq.)	Free Acid Normality	Calculated (H^+) in Pu stock soln. Normality	Pu in Filtrate (mg.)
45.05	0.000	1.020	1.020	1.020	7.4
45.05	0.000	1.035	1.035	1.035	7.5
45.05	2.058	3.091	3.091	1.033	6.8
45.05	2.058	3.101	3.101	1.043	7.5
45.05	4.116	5.152	5.152	1.036	8.2
45.05	4.116	5.171	5.171	1.055	7.9

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