[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

POTENTIOMETRIC TITRATIONS OF PHOSPHATES, ARSENATES AND ARSENITES WITH SILVER NITRATE[1]

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Introduction

Neither Treadwell and Weiss[1a] nor Pinkhoff[2] were able to carry out the potentiometric titration of phosphates and arsenates with silver nitrate. Kolthoff and Furman[3] suggest the use of a buffer solution to keep the hydrogen-ion concentration low enough to cut down the solubility of the silver phosphate and arsenate.

In this investigation various salts of weak acids and stronger bases were used as buffers with varying degrees of success. However, successful results were obtained by using a 0.1 N solution of sodium or potassium hydroxide for a secondary titration to keep the solution at a constant hydrogen-ion concentration. This method gave consistent results with alkali phosphates, arsenates and arsenites and with phosphate rock and arsenate insecticide.

By using a Leeds and Northrup student potentiometer the potentials were measured between silver and normal calomel electrodes.

Materials

Approximately 0.1 N solutions of $AgNO_3$, $NaNH_4HPO_4$, Na_2HAsO_4, Na_2HAsO_3, and NaH_2PO_4 were made and standardized. The $AgNO_3$ solution was standardized by electrolytically depositing the silver;[4] the $NaNH_4HPO_4$ by using a definite weight of the salt; the Na_2HAsO_4 by precipitation and weighing as Ag_3AsO_4;[5] the Na_2HAsO_3 by using a definite quantity of As_2O_3; the NaH_2PO_4 by precipitation and weighing as magnesium pyrophosphate.[6]

Experimental

Sodium bicarbonate[3] and ammonium acid succinate were tried as buffer solutions to neutralize the nitric acid formed during the titration.

$$Na_2HAsO_4 + 3AgNO_3 = Ag_3AsO_4 + 2NaNO_3 + HNO_3$$

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[1] An abstract of theses submitted in partial fulfilment of the requirements for the Degrees of Master of Science at the University of Kentucky, 1928 and 1929.

[1a] Treadwell and Weiss, *Helv. Chim. Acta*, **2**, 680 (1919).

[2] Pinkhoff, "Over de Toepassing der Elektrometrische Titraties," Dissertation, Amsterdam, **1919**.

[3] Kolthoff and Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., New York, **1926**, p. 179.

[4] Edgar F. Smith, "Electro-analysis," P. Blakiston's Son and Co., Philadelphia, **1907**, p. 107.

[5] Georg Lunge and Arnest Berl, "Chemisch-technische Untersuchungsmethoden," 6th ed, **1910**, p. 716.

[6] Treadwell and Hall, "Analytical Chemistry," Vol. II, Quantitative Analysis, John Wiley and Sons, Inc., New York, **1924**, p. 379.

However, silver succinate and silver carbonate seemed to be precipitated and end-points were not obtained. The titration curve showed a break corresponding to excess silver nitrate or silver in solution when the small amounts of nitric acid resulting from the reaction were successively neutralized with 0.1 *N* sodium hydroxide, using one drop of 0.1 *N* phenolphthalein indicator to each 50 cc. of solution. This suggested the use of sodium phenolphthalate as a buffer. In this case the titration curves showed breaks, but varying end-points were observed with different amounts of the buffer.

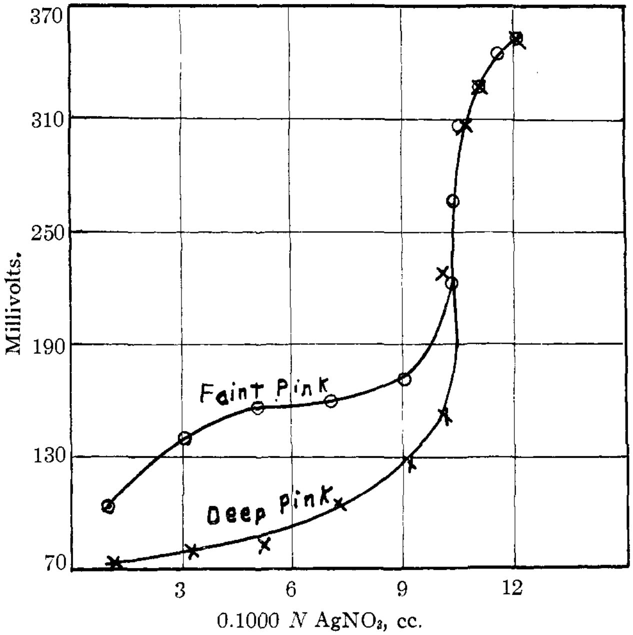

Fig. 1.—Titration curves of two portions of the same solution, one titrated with NaOH until the color of the solution due to the indicator was faint pink; the other until the color was deep pink.

The remaining experimental work was restricted to the use of sodium hydroxide for a secondary titration to the alkaline reaction. The use of the additional buret offered no disadvantage or difficulty. It was not necessary to record the readings of this buret. The solution containing the silver phosphate or arsenite could be neutralized without discontinuing the stirring of the solution. However, as the color of the silver arsenate precipitate is a brick-red, the stirring of the solution was stopped occasionally and the precipitate allowed to settle to make certain that the liquid itself retained a rose-pink color. The volume of the titrated solution was always kept under 300 cc.

Since the question might arise as to whether the sodium hydroxide solution should be added until the phenolphthalein assumed a faint or a deep pink color, the effect on the potential of small variations in the quantity of sodium hydroxide used was studied at different intervals in the titration. While even one drop of 0.1 *N* sodium hydroxide produced considerable change in the potential before the end-point was reached, the effect of an equal quantity immediately after the end-point had been passed was negligible (Fig. 1).

TABLE I

EFFECT OF SODIUM HYDROXIDE AFTER END-POINT

	Arsenate	Arsenite	Phosphate
Initial potential, v.	0.309	0.340	0.3060
After 1 drop 0.1 *N* NaOH, v.	.309	.340	.3060
After 2 drops 0.1 *N* NaOH, v.	.309	.340	.3055
After 3 drops 0.1 *N* NaOH, v.	.308	.339	.3045

Also, in this connection a comparative study was made of the total quantity of silver nitrate required for the various substances when the color of the solution was a faint or a deep pink.

TABLE II

EXPERIMENTAL RESULTS

	Sample, cc.	$AgNO_3$, cc. (faint pink)	$AgNO_3$, cc. (deep pink)
Arsenate	25	25.28	25.33
Arsenite	10	10.08	10.09
Phosphate	10	10.40	10.40

Three slight variations of the drop method were compared. The first variation consisted of adding silver nitrate drop by drop and neutralizing the solution with very dilute (0.01 *N*) sodium hydroxide after

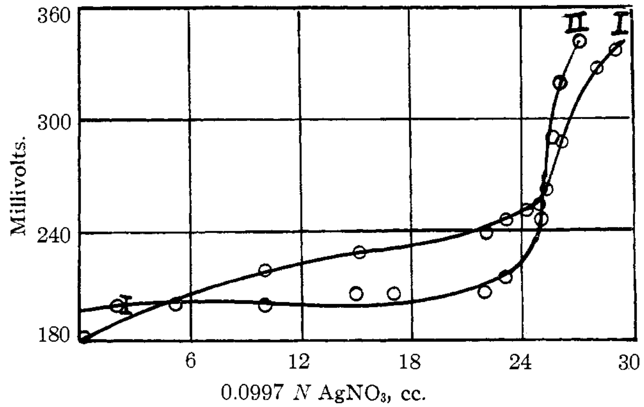

Fig. 2.—Titration curves: I, 25 cc. of 0.1031 *N* NaH_2PO_4; II, 25 cc. of 0.1011 *N* $NaHAsO_4$.

each one or two drops. The second required the addition of a drop of silver nitrate followed by a drop of 0.07 *N* sodium hydroxide. In the third, sodium hydroxide was present in excess before the addition of silver nitrate by drops so that no more sodium hydroxide had to be added.

TABLE III

EXPERIMENTAL RESULTS

(a) Very faint pink solution 0.01 *N* NaOH

$AgNO_3$, cc.	Potential, mv.	d*E*/d cc.
8.95	201	
		3
9.95	204	
		10
10.05	205	
		640
10.10	237	
		460
10.15	260	
		130
10.20	273	

Maximum d*E*/d cc., 10.08 cc.

(b) One drop of $AgNO_3$; one drop of 0.07 *N* NaOH

$AgNO_3$, cc.	Potential, mv.	d*E*/d cc.
9.94	140	
		575
9.98	163	
(after 1 drop NaOH)	141	
		900
10.03	186	
(after 1 drop NaOH)	150	
		1780
10.08	239	
(after 1 drop NaOH)	238	
		520
10.13	264	
(after 1 drop NaOH)	264	
		300
10.16	279	

Maximum d*E*/d cc., 10.06 cc.

(c) Deep pink when first drop of $AgNO_3$ added

$AgNO_3$, cc.	Potential, mv.	d*E*/d cc.
9.45	109	
		84
9.95	151	
		200
10.01	163	
		967
10.07	221	
		732
10.12	265	
		233
10.18	279	

Maximum d*E*/d cc., 10.04 cc.

The results obtained by the potentiometric method have been compared with the results obtained by the standard methods (Table V). In the tables the first column contains the results obtained when using the calculated equivalence potential; the second column, when using the drop method; the third, when using the experimentally determined equivalence potential. The equivalence potentials for these first columns were determined from the solubility products, using the formula[7]

$$E = e_0 - 2.303 \frac{RT}{NF(x + y)} \left(P_{S_{B_xA_y}} - \log \frac{x}{y}\right)$$

where $e_0 = 0.798$ volt for the silver electrode; $T = 294°$ absolute, room temperature; $x = 3$ and $y = 1$, since $xB^{n+} + yA^{m-} = B_xA_y$.

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[7] Ref. 3, p. 71.

TABLE IV

EQUIVALENCE POTENTIALS

	Ag_3PO_4	Ag_3AsO_4	Ag_2AsO_3
Solubility (g. per liter water 20°)	6.4×10^{-3}[a]	8.5×10^{-3}[b]	11.5×10^{-3}[b]
Concn. Ag ion, equiv. per liter	4.61×10^{-5}	5.53×10^{-5}	7.73×10^{-5}
Solubility product	1.54×10^{-18}	3.12×10^{-18}	1.2×10^{-17}
P_S	17.812	17.506	16.923
E (against normal hydrogen elect.)	0.5450	0.5502	0.5579
E of N calomel elect.	0.2871	0.2871	0.2871
E (against N calomel elect.)	0.2579	0.2631	0.2708

[a] Wilhelm Böttger, *Z. physik. Chem.*, **46**, 603 (1903). [b] G. Stafford Whitby, *Z. anorg. Chem.*, **67**, 108 (1910).

Two sets of determinations were made with the microcosmic salt, the second of which was titrated after being boiled with sodium hydroxide. The difference in results is such as might be expected due to the presence of the ammonium group.

TABLE V

RESULTS OF EXPERIMENTS

Sample	taken, cc.	% Error in comparison with standard values when the end-point was determined by		
		Calcd. potential	Drop method	Experimental potential
Na_2HAsO_4	10	0.4	0.3	0.5
	25	0.2	0.1	0.3
Na_2HAsO_3	10	1.1	0.3	0.4
	25	0.4	0.0	0.0
	50	0.5	0.0	0.2
NaH_2PO_4	10	−0.8	1.0	1.2
	25	−1.4	0.8	0.7
$NaNH_4HPO_4$	10	1.0	7.2	7.6
	25	0.3	6.9	7.0
$NaNH_4HPO_4$ (boiled with NaOH)	10	−0.7	1.5	1.5
	25	−0.8	1.7	0.7

A rough comparison between the actual quantities of sodium hydroxide required completely to neutralize the nitric acid formed by the reaction and the theoretical quantities has been made. This comparison shows that a relatively large amount of the sodium hydroxide is used in replacing the ammonium group.

TABLE VI

0.1 *N* SODIUM HYDROXIDE USED FOR 25 CC.

	Experimentally, cc.	Calculated, cc.
0.1011 *N* Na_2HAsO_4	9.2	8.7
0.1000 *N* Na_2HAsO_3	24.7	8.3
0.1000 *N* $NaNH_4HPO_4$	13.3	8.3
0.1000 *N* $NaNH_4HPO_4$ (boiled with NaOH)	18	16.7
0.1031 *N* NaH_2PO_4	18.3	16.7

Since excess sodium fluoride does not interfere with the precipitation of silver arsenate,[8] the calcium in samples of phosphate rock and calcium arsenate insecticide was precipitated with excess sodium fluoride (4%) and the phosphate and arsenate titrated with silver nitrate. In this procedure the nitric acid solution of the calcium phosphate or arsenate was neutralized with sodium hydroxide to the point at which the precipitate just barely redissolved, then the excess sodium fluoride was added and the titration started with silver nitrate. Before the addition of alkali, readings were made until a potential of approximately 0.24 volt was reached, then the sodium hydroxide was added to produce the pink color and the titration continued. By this method all the calcium was precipitated as calcium fluoride instead of calcium phosphate or calcium arsenate and results were obtained which agreed with those from standard methods of analysis of the same samples.

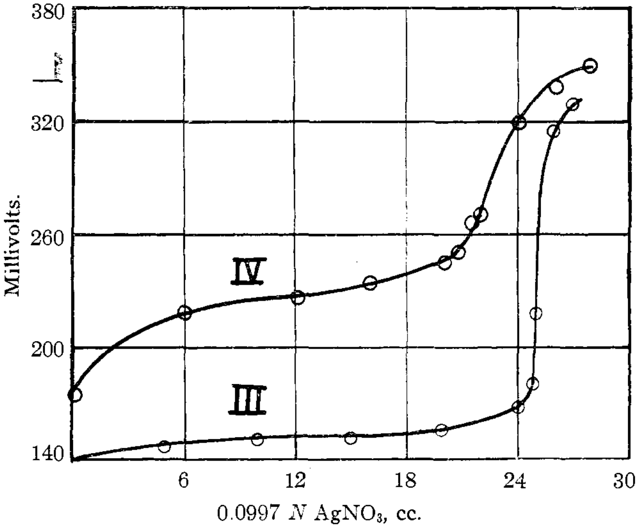

Fig. 3.—Titration curves: III, 25 cc. of 0.1000 N Na_2HAsO_3; IV, 20 cc. of 0.1000 N $NaNH_4HPO_4$.

Summary

The potentiometric titration of phosphates, arsenates and arsenites with silver nitrate has been accomplished by making use of a secondary titration with sodium hydroxide to maintain the desired low hydrogen-ion concentration. The phosphate titration proved the least satisfactory.

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[8] LeRoy W. McCay, THIS JOURNAL, **50**, 368 (1928).