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Amperometric Determination of Trivalent Arsenic in Sulphuric Acid Solution in the Presence of Fluoride Ions

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The polarographic reduction of 1 m*M* $KMnO_4$ at a dropping mercury electrode was studied in H_2SO_4 solutions containing varying amounts of sodium fluoride. The amperometric titration of sodium arsenite with potassium permanganate was carried out at − 0.9 volt (SCE) in acid medium containing fluoride ions that are capable of forming stable fluoride complexes. It was revealed that the titration was successful at 0.028% NaF and 0.54 N H_2SO_4. The effect of $[AsO_2^-]$ revealed suitability of the method for the quantitative determination of very small amounts of trivalent arsenic ranging from 1.5 mg/ml to 1.5 μg/ml.

(Keywords: Trivalent arsenic; Sulphuric acid; Fluoride ions; Amperometry)

Amperometrische Bestimmung von trivalentem Arsen in schwefelsaurer Lösung in Gegenwart von Fluorid-Ionen

Die polarographische Reduktion von 1 m*M* $KMnO_4$ wurde an der tropfenden Quecksilberelektrode in H_2SO_4-Lösungen mit verschiedenem Gehalt an Natriumfluorid untersucht. Die amperometrische Titration von Natriumarsenit mit Kaliumpermanganat wurde bei − 0.9 V (SCE) in saurem Medium in Gegenwart von Fluorid-Ionen, die zur Ausbildung stabiler Fluoridkomplexe befähigt sind, ausgeführt. Die Titration bei 0.028% NaF und 0.54 *N* H_2SO_4 erwies sich als vorteilhaft. Eine quantitative Bestimmung von geringen Mengen von dreiwertigem Arsen als $[AsO_2^-]$ im 1.5-mg- bis 1.5-μg/ml-Bereich ist möglich.

Introduction

The amperometric determination of trivalent arsenic in various supporting electrolytes using $KBrO_3$ [1], I [2] and chloramine-T [3] as titrants has been reported earlier. Procedures for the determination of arsenic in biological materials [4] and in commercial phosphoric acid and sulphuric acid [5], also, have been established. Save for a study involving the potentiometric titration of $NaAsO_2$ with $KMnO_4$ [6], literature is deficient to a study involving amperometric determination of trivalent arsenic in fluoride media using potassium permanganate as a titrant.

Experimental

All chemicals used were of A.R. grade, bidistilled water was used in the preparation of all solutions. Stock 0.0138 N $KMnO_4$ solution was prepared by the method of *Stamm* [7] and standardized with sodium oxalate. For the reaction being examined this normality should be multiplied by 0.8 (change of valency from 7 to 3). 0.0242 N $NaAsO_2$ solution was prepared and standardized by the bromate method [8]. More dilute solutions of either $KMnO_4$ or $NaAsO_2$ were then prepared by accurate dilutions. 2% NaF, 9 N H_2SO_4 and 1% Triton X-100 solutions were also prepared.

The electrolysis cell was as previously described [9]. The diffusion current was measured by a Radiometer PO_4 type polarograph. The capillary characteristics were $m = 1.58$ mg/s and $t = 4.4$ s/drop. The titrated solution was prepared by diluting 1–5 ml of the arsenite solution, 0.35 ml 2% NaF and 0.4–3.0 ml 9 N H_2SO_4 to 25 ml bidistilled water. The applied potential was adjusted at − 0.9 or − 1.15 volts (SCE). The diffusion current corrected for dilution was calculated and plotted against the volume of permanganate. The end point corresponding to the intersection of the two branches of the titration curve was obtained by interpolation.

Results and Discussion

The reaction between arsenite and permanganate in acid solution containing fluoride ions that are liable to form stable manganic fluoride complexes, was investigated in order to define the proper conditions under which the reaction proceeds smoothly according to the following equation:

$$Mn^{7+} + 2\,As^{3+} = Mn^{3+} + 2\,As^{5+}.$$

The polarogram obtained on electrolysing 1 ml $2.42 \cdot 10^{-2}$ N $NaAsO_2$ in a supporting electrolyte solution consisting of 0.35 ml 2% NaF and 1.5 ml 9 N H_2SO_4 diluted to 25 ml with bidistilled water was given in Fig. 1. The two reduction waves obtained are distorted by maxima which were eliminated by the addition of 0.05 ml 1% T. X-100 solution. The limiting currents of the two waves are investigated for the effect of As^{3+} at − 0.9 and − 1.15 volts in order to test their validity for analysis. The two waves were found to obey the *Ilkovic* equation and thus the plot of i_l vs. As^{3+} at − 0.90 volt is linear passing through the origin (Fig. 2).

The results of the amperometric titration of $NaAsO_2$ with $KMnO_4$ in acid medium containing fluoride ions were given in Tables 1 and 2 and represented graphically by the plots in Figs. 3 and 4. In these experiments the different factors which were liable to affect the results of titration were studied. These factors were [NaF], acidity and [As^{3+}].

(i) *Effect of sodium fluoride concentration*

From the foregoing results we were confined to a limited range of sodium fluoride concentration (0.028%). It was revealed that at concen-

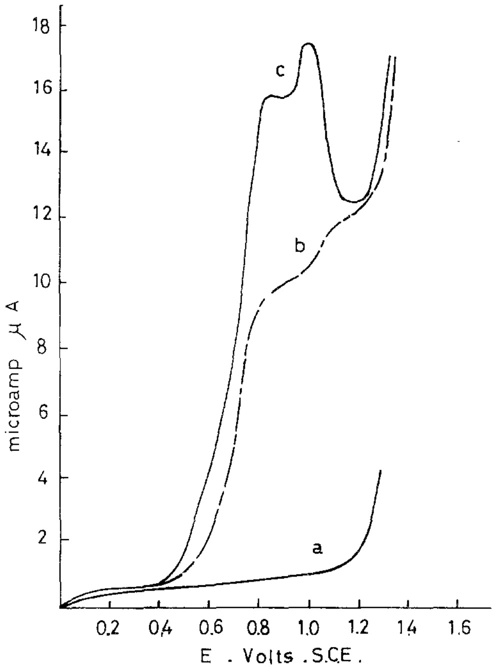

Fig. 1. Polarograms. *a* 0.35 ml 2% NaF + 1.5 ml 9 *N* H_2SO_4/25 ml; *b* soln. (a) + 1 m $121 \cdot 10^{-2}$ M As(III); *c* soln. (b) + 0.05 ml 1% T. X-100

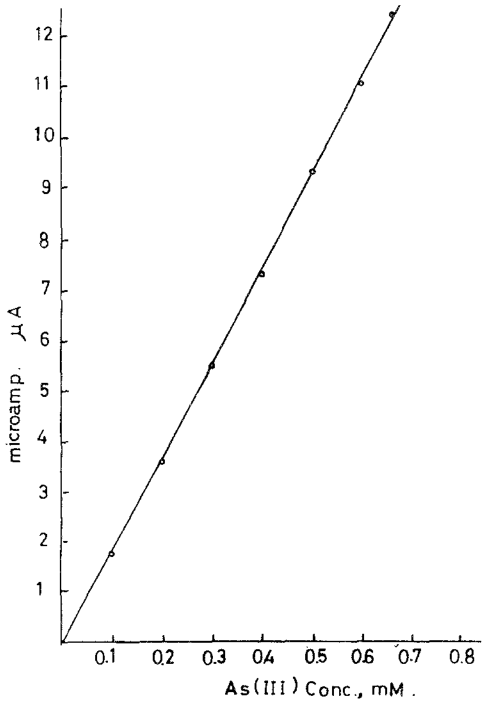

Fig. 2. *Ilkovic* plot

trations lower than 0.028% NaF the reaction becomes very sluggish, shereas at higher concentrations the rate of dropping of the electrode becomes very high and irregular. Accordingly, the concentration of NaF is maintained at a constant value of 0.028%. This concentration was attained by having 0.35 ml 2% NaF per 25 ml solution.

(ii) *Effect of acidity*

The amperometric titration plots of 1 ml 0.0242 *N* $NaAsO_2$ at − 0.9 and − 1.15 volts (SCE) with 0.0110 *N* $KMnO_4$ in presence of 0.35 ml 2% NaF and varying amounts of 9 *N* H_2SO_4 were given in Fig. 3. These plots were normal V-shaped from which the end points were determined by interpolation. The average volumes of the permanganate solution at the end point as obtained from three experiments of each titration were listed in Table 1. These data indicate that good results can be obtained when the acidity is kept at 0.54 *N*. At lower (0.144) and higher (1.08) acidities erroneous results were obtained. At lower acidities the end points were obtained earlier than expected, whereas they were attained later at higher acidities.

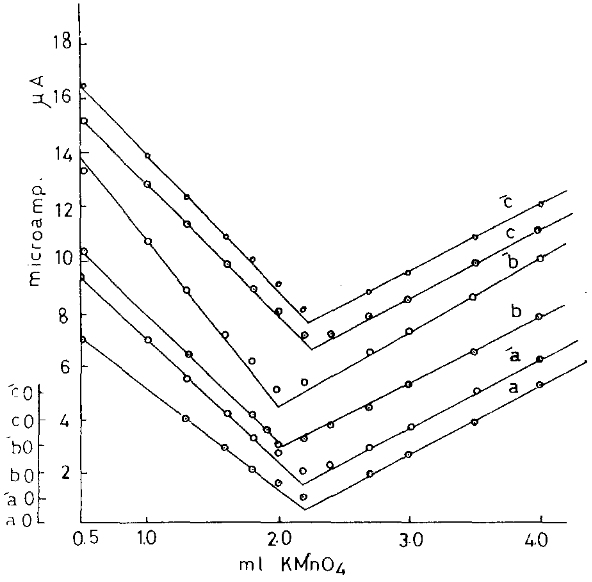

Fig. 3. Effect of acidity (for a legend see Table 1)

Table 1. *Effect of acidity*. Amperometric titration of 1 ml 0.0242 *N* $NaAsO_2$ with 0.0110 *N* $KMnO_4$ in presence of 0.35 ml 2% NaF and varying amounts of 9 *N* H_2SO_4. The solution was completed to 25 ml with bidistilled water

Curve symbol*	9 *N* H_2SO_4 ml	Acidity *N*	Theoretical end point = 2.2 ml	
			ml $1.1 \cdot 10^{-2}$ *N* $KMnO_4$	Error %
a	1.5	0.54	2.2	0.0
a′			2.2	0.0
b	0.4	0.144	2.03	− 7.7
b′			1.99	− 9.5
c	3	1.08	2.25	+ 2.3
c′			2.23	+ 1.4

* a, b and c at − 0.9 whereas a′, b′ and c′ at − 1.15 V (SCE)

(iii) *Effect of* $[As^{3+}]$

The amperometric titration of $NaAsO_2$ with $KMnO_4$ was carried out using solutions of different concentrations of each, viz. $2.42 \cdot 10^{-3}$, $2.42 \cdot 10^{-4}$, $2.42 \cdot 10^{-5}$, and $2.42 \cdot 10^{-6}$ *N*, $NaAsO_2$ and $1.1 \cdot 10^{-2}$, $1.1 \cdot 10^{-3}$, $1.1 \cdot 10^{-4}$ and $1.1 \cdot 10^{-5}$ *N* $KMnO_4$, the process involves titration of 1, 3 and 5 ml at the four concentrations of the arsenite solution at − 0.90 volt and under the proper conditions of acidity (0.54 *N*) and sodium fluoride concentration (0.028%). The titration graphs involving 1 ml of $NaAsO_2$ at the different concentrations were given in Fig. 4. The end points as depicted from such plots were listed in Table 2. The results obtained indicate success of the titration process at the various concentrations used of $NaAsO_2$ since the maximum limit of the errors obtained was ranged between + 0.8 and − 1.5%.

Conclusions

The foregoing results indicate the posibility of amperometric titration of $NaAsO_2$ with $KMnO_4$ in a supporting electrolyte consisting of 0.54 *N* H_2SO_4 and 0.028% NaF. The study reveals the feasibility of determining trivalent arsenic at concentrations ranging from 1.5 mg to 1.5 μg per ml of solution. This appears to be important for determining the element in biological materials in case of arsenic poisoning.

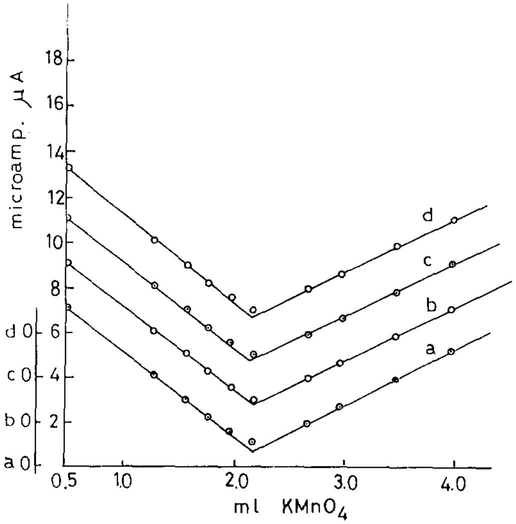

Fig. 4. Effect of concentration. Titration graphs for 1 ml *XN* $NaAsO_2$ + 0.35 ml 2% NaF + 15 ml 9 *N* H_2SO_4 per 25 ml

Plot	a	b	c	d
X N	$2.42 \cdot 10^{-2}$ (μA)	$2.42 \cdot 10^{-3}$ (μA · 10)	$2.42 \cdot 10^{-4}$ ($\mu A \cdot 10^2$)	$2.42 \cdot 10^{-5}$ ($\mu A \cdot 10^3$)

Table 2. *Effect of* [As^{3+}]. Amperometric titration of 1, 3 and 5 ml of *XN* $NaAsO_2$ with *YN* $KMnO_4$ in presence of 0.35 ml 2% NaF and 1.5 ml 9 N H_2SO_4. The solution was completed to 25 ml with bidistilled water

ml AsO_2^- soln.	*XN* $NaAsO_2$ soln.	*YN* $KMnO_4$ soln.	ml $KMnO_4$ soln.	Theoretical E.P. ml	Error %
1.0	$2.42 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$	2.20	2.20	0.0
	$2.42 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$	2.21		+ 0.5
	$2.42 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$	2.17		− 1.4
	$2.42 \cdot 10^{-6}$	$1.1 \cdot 10^{-5}$	2.19		− 0.5
3.0	$2.42 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$	6.60	6.60	0.0
	$2.42 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$	6.65		+ 0.8
	$2.42 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$	6.65		− 0.8
	$2.42 \cdot 10^{-6}$	$1.1 \cdot 10^{-5}$	6.50		− 1.5
5.0	$2.42 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$	11.00	11.00	0.0
	$2.42 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$	11.00		0.0
	$2.42 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$	10.90		− 1.0
	$2.42 \cdot 10^{-6}$	$1.1 \cdot 10^{-5}$	10.85		− 1.3

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