

THE SUCCESSIVE POLAROGRAPHIC DETERMINATION OF
As(III) AND As(V)

by

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INTRODUCTION

Up to the present time no method has yet been described for the successive polarographic determination of As(III) and As(V). This is due to the fact that As(V) has been found not to be reducible in polarography. Only one exception has been found, *viz.* the case in which 11.5*M* HCl was the base solution¹. In this medium a double wave is formed, corresponding to the reduction $\text{As(V)} \rightarrow \text{As} \rightarrow \text{AsH}_3$ and leaving no possibility for a stepwise determination of As(V) and As(III). Moreover, the disadvantage of using this medium is that i_d/c increases with increasing concentration of As(V) above 0.4 *mM*. Hence, for the purpose mentioned in the heading an indirect way was followed.

HEYROVSKÝ² suggested that two polarograms should be recorded: one before and one after reduction of As(V) to As(III) by means of a suitable reducing agent, *e.g.* hydrazine in concentrated sulphuric acid. This agent had already been used by KRJUKOVA for the polarographic determination of As in contact-sulphuric acid³ and phosphoric acid⁴.

As far as the authors are aware of this suggestion of HEYROVSKÝ has never been tried out. We thought it worthwhile to investigate its possibilities. It promised to be attractive because sulphuric acid appears to be the best medium for getting a reasonably developed polarographic diffusion current for As(III)⁵, whereas the reduction of As(V) by hydrazine does not introduce interfering ions into the solution.

EXPERIMENTAL

Stock solutions of As(III) and As(V) were prepared from As_2O_3 and As_2O_5 by dissolving the reagents in NaOH, followed by neutralizing with H_2SO_4 . From these stock solutions different solutions were prepared, all containing 0.01% gelatin as a maximum suppressor and 1*N* H_2SO_4 as a supporting electrolyte.

It has been reported that gelatin is not a suitable maximum suppressor since it causes a reduction of the arsenic wave height⁶, but in accordance with experiments of COULSON⁷, published after our work had been finished, we have not met with any difficulty in our measurements due to using gelatin.

All polarograms were obtained with the automatic pen-recording Radiometer Polarograph type PO 3 using the dropping mercury electrode assembly type E 63. Nitrogen was passed through the solution before each run. The drop time was 2 to 3 sec at room temperature.

The arsenic wave consists of two main parts. The first wave with a half-wave poten-

tial of -0.66 V vs. S.C.E. is directly proportional to the concentration. The second wave is poorly defined, so all data are related to the first wave, half-wave potential and diffusion current being measured as described by WILLARD *et al.*⁹

A typical polarogram of As(III) in $1N$ H_2SO_4 is shown in Fig. 1.

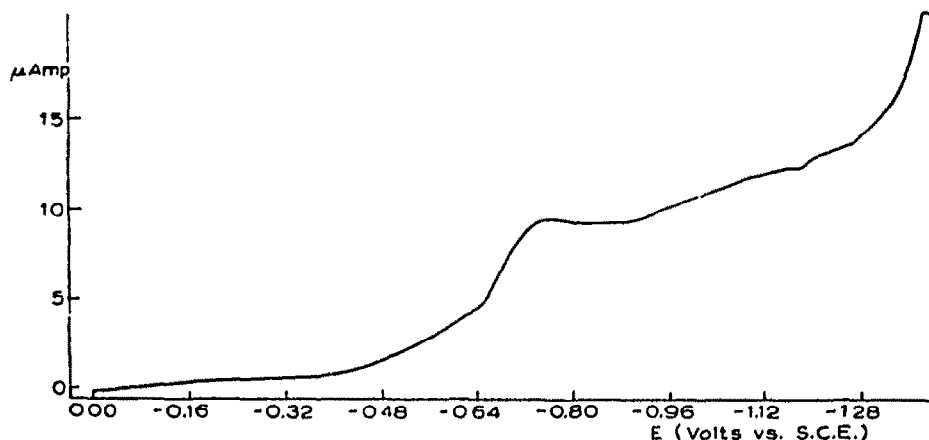


Fig. 1. Polarogram of As(III) Concentration of As(III): $37 \cdot 10^{-6}M$. Supporting electrolyt: H_2SO_4 $1N$. Maximum suppressor: gelatin, 0.01%. Damping: 3. Amplifier sensitivity: 65. Compensation condenser current: 0.

RESULTS

1. Polarograms were recorded of As(III)-solutions with different concentrations. The results listed in Table I show a satisfactory proportionality of i_d with concentration.

2. The influence of hydrazine sulphate and As(V) on the As(III) curves was traced. Hydrazine sulphate (HS) was found to interfere when present in a concentration above 150 mg/100 ml. Above this concentration, the plateau was less pronounced and the wave height decreased. As expected, As(V) had no perceptible influence, not even at a concentration 15 times greater than that of As(III).

3. Preliminary experiments showed that As(V) was reduced by heating with HS in concentrated sulphuric acid. We traced the influence of variations in HS concentration, acid concentration and heating time. The results are listed in Table II. Good results were obtained with about 100 mg HS per 100 ml final solution of at most $10^{-3}M$ As, sulphuric acid concentrations of at least 45% and a heating time of about ten minutes. After reduction the solutions were made $1N$ to H_2SO_4 and 0.01% to gelatin as already noted before.

4. Finally, we determined the total arsenic content of solutions containing known amounts of As(III) and As(V), after reduction had been performed with HS in concentrated H_2SO_4 , by heating for 10 min. Table III shows that the errors are of the same order as those in the determination of As(III).

Remark

Fig. 2 illustrates the calculated inaccuracy of an As(V) determination as a function of the mol % As(V) in a mixture of As(III) and As(V) when the As(V) concentration is found as the difference of two As(III) determinations, one before and one after reduction, each with an inaccuracy of 2%.

TABLE I
 LIMITING CURRENT OF As(III)

No.	As(III) conc $10^{-3}M$	$E_{\frac{1}{2}}$ vs S C E. volt	i_d found μA	i_d calculated* μA	Δ %
1	100	-0.66	26.00	25.68	+ 1.2
2	100	-0.66	25.50	25.68	- 0.7
3	100	-0.66	25.50	25.68	- 0.7
4	100	-0.66	25.50	25.68	- 0.7
5	50	-0.66	12.70	12.84	- 1.1
6	40	-0.66	10.60	10.27	+ 3.0
7	10	-0.66	2.56	2.57	- 0.3
8	10	-0.66	2.61	2.57	+ 1.6
9	4	-0.67	1.03	1.03	+ 0.3
10	1	-0.68	0.15	0.26	-40.0

* Calculated from the data in column 2 and 4 by the method of least squares.

 TABLE II
 REDUCTION OF As(V)

No.	As(V) conc* $10^{-3}M$	H ₂ S conc. mg/100 ml	H ₂ SO ₄ conc. %	Heating time min	$E_{\frac{1}{2}}$ vs. S C E. volt	i_d found μA	As(V) conc. calc. from i_d $10^{-3}M$	Δ %
1	92	50	80	5	-0.66	21.6	84	- 9
2	92	50	80	5	-0.66	21.3	83	-10
3	92	50	80	5	-0.66	21.1	82	-11
4	92	50	80	30	-0.66	22.7	88	- 4.5
5	92	150	80	5	-0.66	20.5	80	-13
6	92	150	80	15	-0.66	21.6	84	- 9
7	92	150	80	30	-0.66	19.4	76	-17.5
8	92	100	80	10	-0.66	23.9	93	+ 1
9	37	100	80	10	-0.66	9.5	37	0
10	37	100	80	10	-0.64	9.6	37	0
11	37	100	80	10	-0.64	9.6	37	0
12	37	100	80	30	-0.64	9.5	37	0
13	92	100	80	30	-0.66	23.9	93	+ 1
14	92	100	70	10	-0.66	23.8	93	+ 1
15	92	100	55	10	-0.66	23.8	93	+ 1
16	92	100	45	10	-0.66	23.9	93	+ 1
17	92	100	35	10	-0.66	18.5	72	-22
18	92	100	30	10	-0.66	13.6	53	-45

* As(V) content of the stock solution determined by titration with Na₂S₂O₃ after addition of KI.

CONCLUSIONS

The polarographic determination of As(III) in 1*N* H₂SO₄ was found possible for concentrations between $10^{-3}M$ and $4 \cdot 10^{-5}M$.

When tolerating a standard deviation of 1.5%, no particular precautions are needed (Table I).

As(V) may be determined within the same concentration limits after reduction by hydrazine sulphate in sulphuric acid of at least 45% by heating at 180-200°C for ten minutes (Table II).

The successive polarographic analysis of As(III) and As(V) may be performed by the method given above. The standard deviation of the results obtained for the total

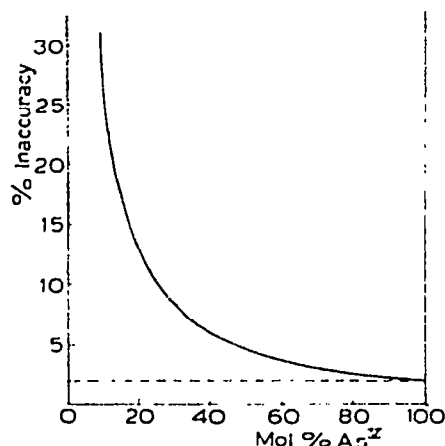


Fig. 2. Inaccuracy of As(V) determination in As(III) + As(V) mixture as a function of mol % As(V)

As content of the mixture is 1.8% (Table III). The inaccuracy in the As(V) content depends on the percentage As(V) of the mixture (Fig. 2).

The determination of both As(III) and As(V) in the same sample is not practical. After recording the polarogram of As(III) one has to acidify the solution strongly for the reduction of As(V), and afterwards to dilute it strongly in order to restore the medium to 1*N*. This may imply an inadmissible decrease of the As concentration. Hence, we recommend separate determinations for As(III) and As(III) + As(V) according to the following procedure:

TABLE III
LIMITING CURRENT OF As(III) + As(V)

No	As(III) conc $10^{-3}M$	As(V) conc $10^{-3}M$	As(III): As(V)	Total As(III) conc after reduction $10^{-3}M$	E_d vs S.C.L. volt	i_d found μA	Total As(III) conc calculated from i_d $10^{-3}M$	Δ %
1	40	37.2	1:1	77.2	-0.67	20.0	77.8	+0.8
2	40	37.2	1:1	77.2	-0.65	19.8	77.1	-0.1
3	80	37.2	2:1	117.2	-0.66	31.6	119.2	+1.8
4	40	74.4	1:2	114.4	-0.67	30.4	118.4	+3.0
5	40	74.4	1:2	114.4	-0.66	30.3	118.0	+3.0
6	40	9.3	4:1	49.3	-0.66	13.0	50.6	+2.2
7	10	37.2	1:4	47.2	-0.66	12.3	47.9	+1.8
8	40	3.7	10:1	43.7	-0.66	11.2	43.7	0.0
9	40	3.7	10:1	43.7	-0.65	11.4	44.4	+1.1
10	100	9.3	10:1	109.3	-0.66	27.7	107.9	+1.0
11	10	93.0	1:10	103.0	-0.66	25.5	101.0	-2.0
12	10	93.0	1:10	103.0	-0.66	25.1	100.0	-3.0
13	4	37.2	1:10	41.2	-0.67	10.8	42.0	+1.9
14	4	37.2	1:10	41.2	-0.65	10.8	42.0	+1.9
15	100	7.4	13:1	107.4	-0.66	27.9	108.7	+1.2
16	8	93.0	1:12	101.0	-0.66	24.4	98.4	-2.5
17	100	3.7	25:1	103.7	-0.65	26.4	102.8	-0.9
18	100	3.7	25:1	103.7	-0.65	26.8	104.4	+0.7
19	4	93.0	1:25	97.0	-0.66	25.2	98.4	+1.5
20	4	93.0	1:25	97.0	-0.66	24.9	97.0	0.0

PROCEDURE

Add to a measured quantity of sample sulphuric acid and gelatin so that the concentrations are respectively between 10^{-3} and $5 \cdot 10^{-5}M$ for As(III), 1N in respect to H_2SO_4 and 0.01% by wt of gelatin. Record a polarogram and determine the limiting diffusion current of the wave with half-wave potential of -0.66 V vs. S.C.E. From this find the As(III) concentration by comparing with standard As(III) solutions.

Add to a second sample as much sulphuric acid and hydrazine sulphate as to obtain a solution of 80% H_2SO_4 with a total As concentration between 28,2 and 1,4 mM and a HS content of about 300 mg/10 ml; heat at 185—200°C for ten minutes. (Should it be difficult to obtain a H_2SO_4 conc. as high as 80%, it is allowed to lower this limit to 45%, provided that the As and HS concentrations are lowered correspondingly.) After cooling dilute to bring the H_2SO_4 concentration to 1N, add the required amount of gelatin and record a new polarogram. From this find the total As concentration as stated above for As(III).

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SUMMARY

A method has been described for the successive polarographic determination of As(III) and As(V) in a 1N sulphuric acid solution.

A directly recorded polarogram shows a limiting current corresponding to the As(III) concentration; another polarogram, recorded with a second sample after reduction of As(V) to As(III) by hydrazine sulphate, gives a limiting current corresponding to the concentration As(III) + As(V)

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