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The Coulometric Titration of Arsenic by Means of Electrolytically Generated Bromine and an Amperometric End-point

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Introduction

A method and apparatus for the determination of thiodiglycol has been described by Sease, Niemann and Swift.[1] This method involved passing a known constant current for a measured time between two platinum electrodes (called the "generator electrodes") immersed in an acetic acid solution containing a soluble bromide, thus at a constant rate generating bromine which oxidized the thiodiglycol. The end-point was obtained by noting the increase in current, caused by excess bromine, between a second pair of platinum electrodes (called the "indicator electrodes") which had a small potential difference impressed across them. The method was developed as part of a war project and time was not available for a detailed study. However, the results obtained, together with the rapidity of the method and the simplicity and cheapness of the apparatus, appeared to justify further investigations in order to establish the accuracy of the method, to obtain a better understanding of certain of the phenomena observed, and to determine the applicability of the method to other constituents. As a part of these investigations a study of the titration of arsenious acid has been made and the results obtained are presented below.

Experimental

Chemicals.—One formal sulfuric acid solutions were prepared from "Reagent Grade" concentrated acid. Immediately after dilution these solutions were found to contain up to 10^{-8} equivalent per milliliter of reducing material; after standing for a day or longer this quantity diminished by 50 to 90%.

Two formal sodium bromide solutions were prepared from "Reagent Grade" material; no reducing material was found present.

Bureau of Standards arsenious oxide was used after being dried for one hour at 115°. Stock 0.005 formal solutions were prepared by dissolving 500 mg. of the oxide in 10 ml. of water containing 1 g. of Reagent Grade sodium hydroxide, then acidifying the solution with 25 ml. of the one formal sulfuric acid and diluting to 500 ml. These solutions were kept for not more than five days.

The laboratory distilled water was found at times to contain as much as 10^{-8} equivalent per milliliter of an oxidizing agent, thought to be chlorine, which could be removed by boiling. A stock of water free of oxidizing agent was used throughout the work.

Apparatus.—The titration cell is outlined in Fig. 1, a basic diagram of the apparatus is shown in Fig. 2, and the details of the electrical circuits are shown in Fig. 3.

The Titration Cell.—The various components of the cell are arranged to give the greatest mechanical strength and to permit the maximum stirring with the minimum fluctuation of solution level; oscillations of the solution level cause variation of the indicator current. Under the conditions of these experiments, changes in the relative positions of the indicator anode and cathode caused no significant difference in the sensitivity of the indicator system. For reasons discussed below the cathode guard shown in Fig. 1 was used to prevent most of the generated hydrogen from being swept into the solution. The small hole in the side of this guard permits sufficient circulation to prevent solution from being trapped in the guard. The amount of hydrogen passing into the solution can be controlled by vertical adjustment of the electrode.

A Cenco variable speed stirrer was used. In order to stabilize the sensitivity of the indicator system the stirrer speed was adjusted by means of a stroboscopic disc consisting of two perpendicular white stripes on a black background illuminated by a fluorescent light or a small neon bulb; a stirrer speed of 1800 r.p.m. was used.

The Indicator System.—All electrodes were made from 0.003 inch platinum foil; the sizes are shown in Fig. 1.

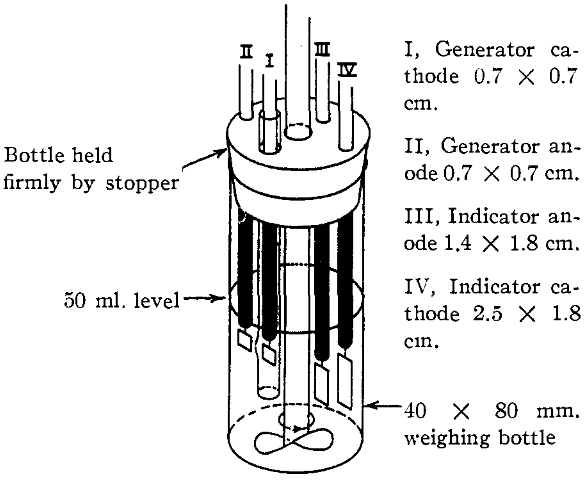

Fig. 1.—Titration cell.

The applied potential difference across the indicator electrodes was usually 200 millivolts. The switch S-8 controlling the sensitivity of the microammeter, M-2, was left in the "high" sensitivity position except in the case of a badly over-run end-point. The switch S-1 was used to short the electrodes during preliminary treatment and storage; otherwise they were found to develop a potential difference.

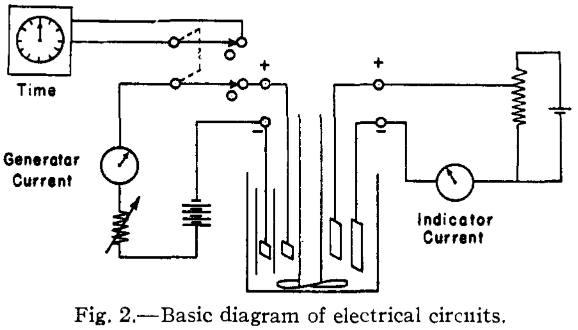

Fig. 2.—Basic diagram of electrical circuits.

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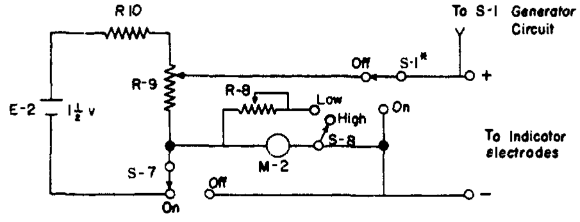
(1) John Sease, Carl Niemann and Ernest H. Swift, *Anal. Chem.*, **19**, 197 (1947).



INDICATOR CIRCUIT

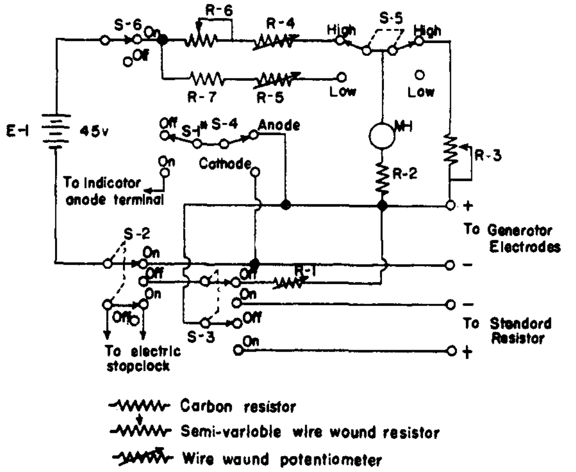


Fig. 3.—Details of generator circuit: *S-1 indicator ganged with S-1 generator: S-1, S-2, S-3, S-5, DPDT radio toggle switches; S-4, S-6, S-7, S-8, SPDT radio toggle switches; M-1 Weston meter, model 301, 0–1 milliampere; M-2 Weston meter, model 301, 0–50 microamperes; E-1 Burgess battery 2308 45v.; E-2 Burgess battery 4F4 1.5v.; R-1 3000Ω, R-2 600Ω2w, R-3 350Ω10w, R-4 1500Ω, R-5 15,000Ω, R-6 5000Ω10w, R-7 45,000Ω2w, R-8 2000Ω10w, R-9 100Ω10w, R-10 240Ω2w.

The indicator anode size is not important. The sensitivity of the indicator system depends linearly on the size of the cathode.

The Generator System.—The switch S-5 provides for "high" and "low" bromine generating rates of approximately 10 and 1 milliamperes, respectively, corresponding to 10^{-7} and 10^{-8} equivalent per second. The generating rate could be adjusted within a reproducibility of ±0.05% by making use of a fixed point near the 10 milliampere calibration on the scale of meter M-1; calibrations over a ten minute period were found to agree to within ±0.1%. With batteries in good condition the current through a fixed resistance would normally remain constant to within ±0.1% over a ten minute period.

Because of temperature and other variations the current value for a specific setting was checked every ten minutes by setting the calibration switch, S-3, to the "on" position and measuring the potential across a standard 200 ohm resistance by means of a potentiometer.

The switch controlling bromine generation, S-2, was ganged so that a Standard Electric Time Co., model S-10, time clock, calibrated to one-tenth second was started and stopped with the generation current.

Resistance R-1 was provided so that between consecutive titrations and during the "warm up" period the current through the meter and battery would be the same as during a titration; this resistance has to be adjusted to correspond to the generation rate. Resistance R-2 was provided so that the contact resistance of switch S-5 had little effect on the resistance in shunt with milliammeter, M-1; switch S-5 has to be of better quality than the other switches.

Accuracy of Standards and Measurements.—The absolute accuracy of the current determination was dependent upon the accuracy of the standard resistor and the standard cell used. The resistance was a 200 ohm coil from a Leeds and Northrup no. 4716 resistance decade, rated by the manufacturer as ±0.05%.[2] The standard cell used was checked against a Weston standard cell which had been calibrated by the U. S. Bureau of Standards; however, during the period of its use the value of the cell changed 1 millivolt. Therefore the uncertainty in the current determination was ±0.1%. The error in the potentiometer readings should have been less than ±0.1%.

The errors in the preparation of the solutions and in the volumetric measurements involved are believed to be less than ±0.1%.

The value used for the faraday was 96,500 coulombs.

Procedure.—When not in use the electrodes are immersed in a solution prepared from 5 ml. of 1 *F* sulfuric acid, 5 ml of 2 *F* sodium bromide and 40 ml of water; the switch S-1 should be in the "on" position. This procedure minimizes changes in the sensitivity of the indicator electrodes and the development of potential differences between them.

First the apparatus is allowed to equilibrate for ten minutes with S-6 and S-7 on, with S-2 and S-3 off, with S-5 set for the appropriate rate, and with R-1 set to the approximate cell resistance for that rate. (After this period the voltage of the generator battery should have become constant and the reading of M-1 stable.) Then before use after a period of storage the electrodes are treated as follows: With switch S-1 on, the generator switch S-2 is turned on for an arbitrary time of nine seconds (at either rate); during this time the treatment selector switch, S-4 is turned to the "cathode" position for three seconds and to the "anode" position for six seconds.

Because the sensitivity of the indicator electrodes tends to change, end-point correction measurements are then made. These values are obtained by generating bromine in the titration medium, at the rate to be used in the titration, for five periods (one or five seconds each for the high or low rate, respectively) and noting the microammeter reading when the needle becomes stable after each of these periods. The stirrer speed should be checked after each period. Two series of such measurements are made. These readings should agree within 3 microamperes at currents of 40 microamperes. Each reading should be stable for twenty seconds and at 40 microamperes momentary fluctuations of the needle should not exceed 1 microampere. With proper reagents the initial current, zero generation time, should not exceed 1 microampere. After completion of each of the end-point correction measurements the indicator electrodes are again treated in the anode position for five seconds as directed above. In Figure 4 the data obtained from a series of three such measurements made on the low generation rate have been plotted in order to show the reproducibility of the measurements and the linearity of the current-time curve. At the high generation rate the end-point correction time is of the order of 1% of the titration time, therefore if the indicator system is reproducible to within ±10%, the uncertainty introduced into the titration should not exceed ±0.1%.

The switch S-3 is then turned on and the desired setting of M-1 calibrated for its exact current value. This calibration should be made every ten minutes or at the end of every titration.

The titrations were made by pipetting the arsenite solu-

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[2] Not until after the termination of this investigation did a resistance standard become available, a Wolff potentiometer calibrated to within 0.01%. The 200 ohm. coil was then checked against this standard, and was found to be 0.06% low. Since this correction opposed a possible hydrogen current correction, mentioned later, of 0.1% or less, the uncorrected value of 200.0 ohms was used in the calculations.

tion into the titration cell, which contained 5 ml. of 1 *F* sulfuric acid and 5 ml. of 2 *F* sodium bromide, and then diluting the solution to 50 ml. Generation at the appropriate rate is then begun and continued until the first sign of a definite decrease or increase in the indicator current. If the indicator current is less than 2 microamperes, generation is continued until it becomes greater than this value. The indicator current at the end-point should be less than 40 microamperes for the high generation rate and less than 20 microamperes for the low rate. The end-point correction in seconds is obtained by interpolation between the values obtained from the end-point correction measurements.

After each titration the indicator electrodes are treated as was done after the end-point correction measurements, use being made of the titrated solution.

Discussion of the Method

Limitations.—The predominant reaction at the generator anode is the oxidation of bromide to bromine, and at the cathode the reduction of hydrogen ion. One would predict that the method as described would be limited in application to substances which do not establish reversible electrode potentials, otherwise there would be appreciable reduction at the generator cathode of the oxidation product and also the possibility of significant current flow through the indicator system throughout the titration. Also, the assumption is made that the oxidation of hydrogen gas at the generator anode is not a significant factor in the total current through the generator circuit. The results obtained show that in the solution used the arsenic in the quinquepositive state is inert to the generator cathode and to both indicator electrodes. The possibility of extending the method to substances which establish reversible electrode potentials by isolating the generator cathode and by modifications of the end-point procedure is being investigated.

Indicator Current Phenomena.—In solutions 0.1 *F* in sulfuric acid, 0.2 *F* in sodium bromide and varying from 5 to 50 $\times$ 10^{-7} *F* in bromine, this bromine concentration corresponding to indicator currents of from 5 to 50 microamperes, the predicted indicator electrode reactions could be represented as

$$\text{Cathode}\quad Br_2 + 2e^- = 2Br^-$$
$$\text{Anode}\quad 2Br^- - 2e^- = Br_2$$

Making use of a saturated calomel cell and salt bridge, measurements were made (under the conditions of an end-point correction measurement) of the potentials of the generator cathode, generator anode, and of an independent platinum electrode immersed in two such solutions. The values obtained are summarized in Table I.

TABLE I

POTENTIALS OF THE INDICATOR ELECTRODES

Indicator current, microamperes	Potential difference (volts) of indicator electrode *vs.* S. C. E. cathode	anode	Potential difference (volts) of solution. *vs.* S. C. E.
11	0.50	0.71	0.70
30	.53	.73	.71

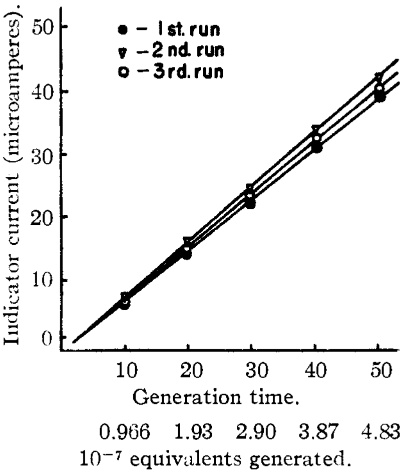

Fig. 4.—Reproducibility of end-point correction measurements: solutions prepared from 5 ml. of 1 *F* sulfuric acid and 5 ml. of 2 *F* sodium bromide diluted to 50 ml.; titrated on the low rate at 0.932 milliampere: ●, first run; ▽, second run; ○, third run.

It appears that the indicator current in the system described is limited by the diffusion of bromine to the cathode. The following formula for such a diffusion current has been derived by Laitinen and Kolthoff[3] with the aid of Fick's law

$$i = (AD/l)\ nFc$$

Here i is the diffusion current, A is the area of the electrode, D is the diffusion constant for the diffusing substance, l is the thickness of the diffusion layer, n is the number of electrons involved, F is the Faraday, and c is the concentration of the diffusing substance in solution.

From this formula it can be seen that an increase in the area of the cathode should increase the bromine diffusion current. This was observed by Sease, Niemann and Swift.[1] Also the current should be a linear function of the bromine concentration, and Fig. 4 shows this to be true. Also one would expect that stirring the solution would decrease the thickness of the diffusion layer, thereby increasing the sensitivity.

Laitinen and Kolthoff[4] used a rotating microcathode (at 600 r. p. m.) with a total surface area of 0.047 sq. cm. and obtained a sensitivity of 1.77 microamperes/10^{-5} mole of Br_2/liter. Using a cathode with a total surface area of 9.0 sq. cm. and the stirring means described we obtain a sensitivity of 1.0 microamperes/10^{-7} mole of Br_2/liter.

The Effect of Hydrogen Gas.—In the apparatus used by Sease, Niemann and Swift[1] the hydrogen produced at the generator cathode was swept into the solution. During a titration the indicator current was found to increase slowly, and before the end of a two-hundred second

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(3) H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1061 (1941).

(4) H. A. Laitinen and I. M. Kolthoff, *ibid.*, **45**, 1079 (1941).

titration the current would have become 10–30 microamperes. Shortly before the equivalence point of the titration the current would begin to decrease, would reach zero, reverse direction and temporarily a meter reading below zero would be obtained; then after a few seconds the meter reading would increase rapidly. This decrease and reversal are hereinafter called the **Current Decrease** and the **Current Reversal.**

If hydrogen is bubbled into a solution such as is used for end-point corrections the indicator current will rise, apparently because of oxidation of hydrogen gas at the indicator anode and simultaneous reduction of hydrogen ion at the indicator cathode. However, when bromine generation is started the current will behave as described above. The data from two such experiments are illustrated in Fig. 5.

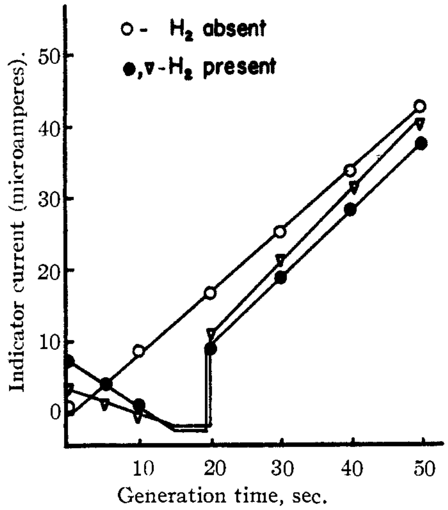

Fig. 5.—The effect of hydrogen gas on end-point correction measurements: solution prepared from 5 ml. of 1 *F* sulfuric acid and 5 ml. of 2 *F* sodium bromide diluted to 50 ml. The hydrogen was bubbled into the solution till the current indicated at zero time was obtained, then bromine was generated in five to ten second intervals and the value of the current read five to fifteen seconds after termination of generation. Portions of curves between ten and twenty seconds describe the general behavior of the meter during this period. Generation rate was 0.90 milliampere.

It is evident from the figure that if hydrogen were present at the end-point, and the normal end-point correction made, the titration would give high results. This is illustrated by the titration graph shown in Fig. 6.

A series of titrations was run (as illustrated in Fig. 6) in which the hydrogen produced at the generator cathode was allowed to pass into the solution. When the normal end-point correction was used the results were 1% too high; when nitrogen was bubbled into the solution to eliminate the dissolved hydrogen, the few measurements made were within 0.3%. The use of nitrogen was not investigated further, since by the use of the cathode shield satisfactory results and certain advantages were obtained.

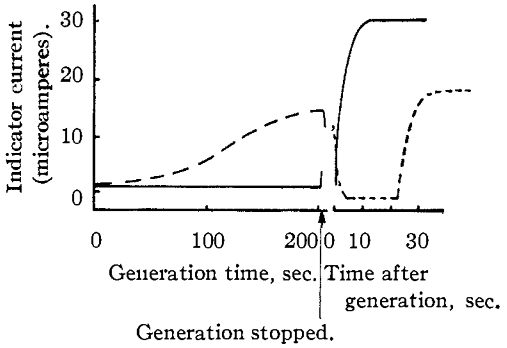

Fig. 6.—Titration characteristics with and without hydrogen present: the solid line represents a titration in which hydrogen was excluded from the solution; the dashed line represents a titration in which hydrogen was allowed to accumulate. The flat portion of the dashed curve represents time during which the meter needle is held fixed below zero by reversal of current. Solution was prepared from 5 ml. of 1 *F* sulfuric acid, 5 ml. of 2 *F* sodium bromide, and 10 ml. of 2×10^{-3} *N* arsenite solution diluted to 50 ml.; generation rate, 9.65 milliamperes.

Since the area of the generator anode is approximately one fifth that of the indicator anode, and the maximum concentration of hydrogen in the solution is obtained only near the end-point, it has been assumed that the error caused by oxidation of hydrogen at the generator anode is relatively small.

Current Decrease.—Kolthoff and Miller[5] have described the action of the polarograph in a solution exhibiting what they term a "mixed potential." Solutions containing hydrogen and bromine have been found to have such a potential, and the explanation advanced by Kolthoff and Miller for the current–voltage phenomena with a single electrode system can be applied to our two electrode system. According to this explanation the time of zero current should correspond to equal quantities of hydrogen and bromine diffusing to an electrode in the solution.

In Figure 5 the measurements obtained from end-point correction experiments with and without hydrogen are plotted. It is seen there that the number of equivalents per second of hydrogen diffusing to the anode can be calculated by the initial indicator current, and at zero current the amount of bromine which has been generated would in the absence of hydrogen, cause a diffusion current which is represented by the normal end-point correction curve. On this normal curve, this current would represent the number of equivalents per second of bromine diffusing to the cathode at the time of zero current. In Table II such values are calculated for the amount of hydrogen and bromine arriving at 1 sq. cm. of electrode surface per second at zero current for different values of initial hydrogen current.

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[5] I. M. Kolthoff and C. S. Miller, THIS JOURNAL, **62**, 2171 (1940).

TABLE II

THE EFFECT OF HYDROGEN GAS

I_{H_2}[a] microamperes	N_{H_2}[b] 10^{-11} eq.	I_{Br_2}[c] microamperes	N_{Br_2}[d] 10^{-11} eq.
1.8	0.37	3.0	0.35
4.0[e]	0.83	7.9	0.91
4.3	0.90	7.8	0.90
5.0	1.1	8.3	0.95
7.4[e]	1.5	9.3	1.1
13.0	2.7	21.0	2.4
15.0	3.1	18.0	2.1

[a] I_{H_2}, initial hydrogen current. [b] N_{H_2}, equivalents of hydrogen arriving at 1 sq. cm. of anode per second for I_{H_2}. [c] I_{Br_2}, bromine current at time of zero current if no hydrogen were present. [d] N_{Br_2}, equivalents of bromine arriving at 1 sq. cm. of cathode per second for I_{Br_2}. [e] Note: I_{H_2} of 4.0 and 7.4 are taken from Fig. 5, other values are from unpublished measurements.

It can be seen that at the lower values of hydrogen current, when the rate at which the hydrogen leaves the solution is small, the calculated values of bromine and hydrogen which arrive at an electrode are approximately equal at the time of zero current.

Current Reversal.—In the upper portion of Fig. 7 the potential of the indicator cathode *versus* a saturated calomel half cell is shown during generation of bromine with and without hydrogen being initially present in the solution.

As would be expected, during the period of current decreases and current reversal there is a great change in the potential of the indicator electrodes and of the solution. If because of a local condition about one of the indicator electrodes the potential of that electrode were to lag or lead the potential of the other electrode during this change, a transient condition could exist whereby the potential between the indicator electrodes could be greater than the applied potential, thus causing a reversal of current.

During hydrogen diffusion current, before the addition of bromine, hydrogen is being produced at the indicator cathode and being removed at the indicator anode. One might expect then that at the time of zero current, when equal quantities of bromine and hydrogen are arriving at the anode, there would be an adsorbed layer of hydrogen on the indicator cathode. A cell would then be established in opposition to the applied potential, and could cause a current reversal until this hydrogen was removed. Thereafter bromine predominates at the cathode and the current behaves essentially as during bromine generation in the absence of hydrogen.

It is of interest to note that the number of equivalents of hydrogen which would be discharged to cause the current reversal as illustrated in Fig. 6 would be about 4 × 10^{-10} equivalent. A monomolecular layer of hydrogen on the 9.0 sq. cm. cathode, assuming one hydrogen molecule per 10 Å.^{2}, would amount to 3.0 × 10^{-8} equivalent.

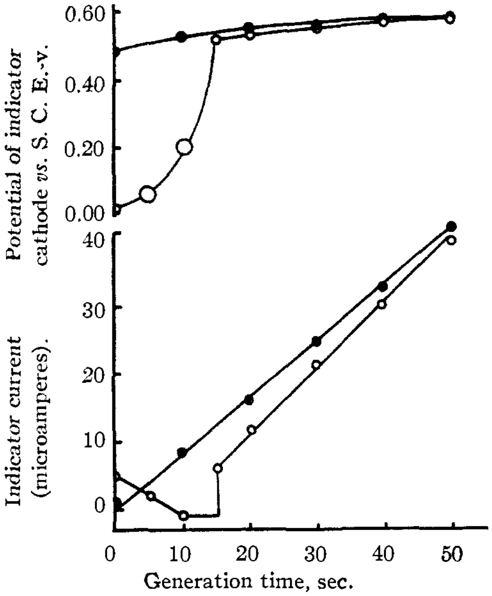

Fig. 7.—Change of potential of indicator cathode during generation (with and without hydrogen): solution prepared from 5 ml. of 1 *F* sulfuric acid and 5 ml. of 2 *F* sodium bromide, diluted to 50 ml.; generation rate, 0.90 milliampere: ●, hydrogen absent; ○, hydrogen present.

Titration of Arsenite Solutions.—In Table III are shown the data collected from a series of titrations of arsenious acid solutions in which there was no guard tube over the generator cathode and in which the hydrogen evolved was allowed to pass freely into the solution. The error is in all cases positive and is attributed to the hydrogen effect discussed above.

TABLE III

TITRATIONS OF ARSENITE SOLUTIONS (NO GUARD TUBE OVER GENERATOR CATHODE)

The arsenious acid was added to 5 ml. of 1 *F* sulfuric acid and 5 ml. of 4 *F* potassium bromide, then the volume was adjusted to 50 ml. In all cases current decrease and current reversal were obtained; the indicator current at the beginning of current decrease varied from 20–40 microamperes.

				Arsenic, micrograms		
Expt.	Generation time, sec.	Generator current, milliamperes	End-point correction, sec.	Taken	Found	Error
Ia	199.8	9.77_0	6.4	726.3	733.4	7.1
Ib	198.3	9.77_0	5.0	726.3	733.0	6.7
IIa	249.7	9.68_0	3.5	919.1	925.0	5.9
IIb	249.1	9.68_0	3.0	919.1	924.6	5.5
IIIa	392.2	9.72_0	3.6	1452.5	1466.1	13.6
IIIb	390.6	9.72_0	3.0	1452.5	1462.3	9.8

A series of titrations was run using the apparatus with the guard shown in Fig. 1 around the generator cathode. During a two-hundred second titration the cathode guard permitted sufficient hydrogen to pass into the solution to give an indicator current of about 1.2 microamperes just before the end-point. This hydrogen diffusion current was adequate to give a small decrease and a distinct current reversal. Since on the high rate bromine is being generated at such a rate as to cause an indicator current rise of 10 microamperes per second after passing the equivalence-point it was decided that the current reversal, especially for an inexperienced operator, was a convenient end-point indication, and at times resulted in a smaller end-point correction.

From the above discussion of the current decrease, it is seen that 1.2 microamperes of hydrogen diffusion current would correspond to a decrease of 2.2 microamperes in the bromine diffusion current at the end-point. For a two-hundred second titration this would be a correction of −0.10%. Since the accuracy of the standards is of this magnitude, this correction was not used. Therefore, in the calculation of the values of arsenic found shown in Table IV no hydrogen correction was made.

TABLE IV

TITRATIONS OF ARSENITE SOLUTIONS (GUARD TUBE OVER GENERATOR CATHODE)

The arsenious acid was added to 5 ml. of 1 *F* sulfuric acid and 5 ml. of 2 *F* sodium bromide, then the volume was adjusted to 50 ml.

Generation time, sec.	Generator current, milli-amperes	End-point corrn., sec.	Arsenic found, micrograms	Error
Solution I—860.3 micrograms of arsenic taken				
227.1	9.81_0	1.3	859.7	−0.6
226.5	9.82_0	0.9	859.9	− .4
227.0	9.83_5	1.7	860.0	− .3
227.1	9.83_5	1.8	860.0	− .3
			Average 859.9	−0.4
Solution II—800.0 micrograms of arsenic taken				
210.4	9.82_5	0.7	799.7	−0.3
210.5	9.82_5	0.7	800.1	.1
211.0	9.82_0	1.0	800.4	.4
210.5	9.82_0	0.6	800.0	.0
			Average 800.1	0.1

In order to demonstrate the general accuracy of the method, another series of titrations was run. In this case the first member of each set was an unknown for the operator. The operator knew only that the end-point would not occur during the first thirty seconds of the titration period. This allowed him to correct for the initial fluctuations in the generator current. Two operators were used, one of the authors (RM) and an inexperienced operator. (We are indebted to Mr. W. S. Wooster for making these determinations.)

A good current reversal was obtained, in the titrations made on the high rate which were longer than one-hundred seconds; those made on the low rate gave no current reversal. The results of this series of determinations are tabulated in Table V. An inspection of this table shows that the absolute error appears to be independent of the amount of arsenic being determined, that the maximum deviation is about 1 microgram, and the average deviation is 0.5 microgram.

TABLE V

TITRATIONS OF ARSENITE SOLUTIONS (GUARD TUBE OVER GENERATOR CATHODE)

The arsenious acid was added to 5 ml. of 1 *F* sulfuric acid and 5 ml. of 2 *F* sodium bromide, then the volume was adjusted to 50 ml.

Expt.	Operator	Generation time, sec.	Generator current, milli-amperes	End-point corrn., sec.	Arsenic, micrograms Taken	Found	Error
Ia	M	252.3	9.83_5	0.4	960.4	961.6	1.2
b		252.3	9.83_5	0.7	960.4	960.4	0.0
c		252.2	9.83_5	0.5	960.4	960.8	0.4
IIa	W	211.8	9.80_5	1.4	800.4	800.7	0.3
b		210.9	9.80_5	0.6	800.4	800.3	−0.1
c		210.9	9.80_5	1.0	799.7	798.8	−0.9
IIIa	W	112.1	9.82_5	2.9	416.5	416.4	−0.1
b		109.7	9.82_5	0.4	416.5	416.8	0.3
c		110.5	9.82_5	1.2	416.5	416.8	0.3
IVa	M	85.3	9.83_0	1.5	320.6	319.7	−0.9
b		86.4	9.83_0	2.3	320.6	320.9	0.3
c		85.7	9.83_0	1.8	320.6	320.1	−0.5
Va	W	247.2	0.930	7.6	86.2	86.5	0.3
b		247.3	0.930	8.0	86.2	86.4	0.2
c		253.0	0.930	12.1	86.2	87.0	0.8
VIa	W	175.8	0.930	6.1	60.4	61.3	0.9
b		175.0	0.930	6.4	60.4	60.9	0.5
VIIa	M	103.8	0.930	6.3	34.5	35.2	0.7
b		102.8	0.930	6.1	34.5	34.9	0.4

Summary

A coulometric method is described for the determination of approximately 30–1000 microgram quantities of tripositive arsenic. The arsenic is oxidized by electrolytically generated bromine, and an amperometric method is used for the determination of the end-point. The accuracy of this amperometric method has been improved by limiting the amount of hydrogen passing into the solution from the generator cathode. The causes of the decrease and reversal of the indicator current near the equivalence-point have been investigated.

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