THE COULOMETRIC TITRATION OF IODIDE WITH ELECTROLYTICALLY GENERATED BROMINE USING AN AMPEROMETRIC ENDPOINT

BY

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Introduction:

A method and apparatus for the amperometric titration of thiodiglycol was developed by Sease, Niemann and Swift[6]. In this method thiodiglycol was oxidized by means of electrolytically generated bromine, and the end point determined by observing the current flow between two platinum indicator electrodes which have a small potential difference impressed between them. By measuring the time of bromine generation and current flow during generation, the number of equivalents of bromine generated was determined.

Further study of this method was made by Myers and Swift[5] who applied it to the determination of tripositive arsenic. Neither thiodiglycol, tripositive arsenic nor their oxidation products react with the generator cathode or the indicator electrodes. Accordingly, no significant indicator current flows between the indicator electrodes until the titration endpoint has been reached. By shielding the generator cathode and by modification of the titration procedure, it should be possible to extend this method to substances which establish reversible electrode potentials.

An example of such a substance is iodide ion. A study has been made of the indicator current flow characteristics during the oxidation of iodide to iodine monobromide, and a method for the analysis of small quantities of iodide has been developed.

Reagents:

Six formal hydrochloric acid solutions were prepared from "Reagent Grade" concentrated acid. The acid available commercially was found to contain as much as 3.5×10^{-8} equivalents of reducing agent per milliliter. The amount of reducing agent present was determined by electrolytic oxidation and was removed by boiling the six formal acid with the calculated amount of 3% hydrogen peroxide. If too much peroxide were added, the excess was destroyed by boiling for about fifteen minutes.

One formal sodium bromide solutions were prepared from "Reagent Grade" salt. These solutions, when tested, were found to contain no unwanted oxidizing or reducing agents.

On occasions, laboratory distilled water was found to contain as much as 10^{-6} equivalents per liter of an oxidizing agent, presumably chlorine. This was conveniently removed by bringing the water to a boil, bubbling clean, dry air thru it while it was being heated.

Stock tenth formal solutions of potassium iodide were made up by weight from "Reagent Grade" salt which had been dried for one hour at 110 deg. C. The potassium iodide used was found to contain no iodate. The solutions were made 0.01 F in sodium carbonate to prevent air oxidation. Dilutions of the stock solutions, 0.005 F in sodium carbonate, were used directly for titrations.

Apparatus:

The apparatus used was essentially that employed by Myers and Swift[5]. The titration cell contains four electrodes made from 0.002" platinum foil, two generator electrodes each 1/2 cm^2 in area, an indicator anode 3.15 cm^2 in area, and an indicator cathode 5.46 cm^2 in area. The generator cathode was contained within a glass shield, terminating in a sintered glass disc thru which contact with the solution was made. By keeping this shield filled with six formal hydrochloric acid, the generator cathode was effectively insulated from the solution. This protection removed the danger of reduction of oxidation products at the generator cathode and eliminated any indicator current due to the presence of hydrogen in solution. The sample to be titrated was placed in a 40 x 80 mm weighing bottle, which was then fitted to a rubber stopper thru which the electrodes and stirrer passed.

During a titration the solution was stirred continually by means of a Cenco variable speed stirrer, turning at 1800 rpm. This speed was determined and maintained constant by means of a stroboscopic device mounted on the stirrer. It was found necessary to run the stirrer for fifteen minutes before constant speed was attained.

A diagram of the indicator and generator circuits is given in figure 1. In the indicator circuit a small potential (usually 138 millivolts in these experiments) is impressed across the indicator electrodes. Any current flowing between the electrodes is registered on a microammeter. In the generator circuit a choice of two rates of bromine generation is possible. On the high rate a current of approximately 10 milliamperes flows thru the generator electrodes; on the low rate a current of approximately 1 milliampere flows. Current flow is determined by measuring the potential drop across a standard 200 ohm resistance by means of a potentiometer. The resistance used was calibrated by means of a Wolff potentiometer and has a value of 199.87 ohms ± 0.03%.

Procedure:

When not in use, the electrodes were stored in a solution two formal in hydrochloric acid and one tenth formal in sodium bromide. Before use, the indicator electrodes were shorted together and made the generator anode, and bromine was generated on their surfaces for a short period of time. This treatment was found to increase the stability of electrode sensitivity. In some cases when the electrodes had been used for antimony or arsenic determinations, it was found advisable to generate hydrogen on their surfaces for a short period of time, and then bromine for a longer period of time (up to 50 seconds.)

Sensitivity of the indicator electrodes, in microamperes of indicator current per second of bromine generation, at the appropriate rate was determined each day by generation of bromine for a certain length of time and recording of the indicator current. On the high rate, three seconds generation gave an indicator current of about 30 microamperes; on the low rate, thirty second's generation gave an indicator current of about 26 microamperes. Indicator current has been observed to be a linear function of the bromine concentration at constant values of acid and bromide concentration. For this reason it was necessary to determine the sensitivity under the particular conditions of concentration which were to obtain during the subsequent titrations. Daily determination of sensitivity was necessary, because it was found that the sensitivity dropped somewhat from day to day (from 11.2 microamperes per second to 10.0 microamperes per second in two weeks, for example.) This drop in sensitivity was not constant, and the sensitivity was observed to improve when the electrodes were not used for several days.

To make a determination, a sample of the iodide solution was pipetted into a 40 x 80 mm weighing bottle and diluted to give a solution of 50 ml, two formal in hydrochloric acid and one tenth formal in sodium bromide. Neither the acid concentration nor the bromide concentration was found to be critical, if the sensitivity were previously determined at the concentration used. An acid concentration of two formal and a bromide concentration of one tenth formal were used in this work.

After the initial diffusion current was determined, the indicator circuit was opened and generation started. When the approximate concentration was known, the indicator circuit was closed about ten seconds before the end point. In the titration of an unknown sample, it was necessary to take trial readings of the indicator current during the course of a titration. After the point of maximum current has been reached, two readings will give a rough indication of the location of the end point.

The point at which a minimum indicator current passed was noted, and generation was allowed to proceed until an indicator current of 25 to 40 microamperes was obtained. Generation was then stopped and the time and indicator current recorded. After each titration the indicator electrodes were treated as indicated above, and the generation current was determined. On the high rate, the potential across the standard resistance varied a few millivolts (from 2.036 to 2.040 volts, for example) during the course of an afternoon. Readings were taken after each titration, and an average value used for the series of titrations. On the low rate, the potential across the standard resistance had a constant value from day to day (0.190 volts.) This was verified at the start and finish of each series of titrations. End point correction was made by extrapolation of the final indicator current to zero current, using the previously determined indicator electrode sensitivity.

<u>Discussion</u>:

During the course of a titration in a solution two formal in hydrochloric acid and one tenth formal in sodium bromide, iodide is oxidized first to iodine and then to iodine monobromide (since the iodine - iodine monobromide potential, -0.87 v is less negative than the iodine - iodine monochloride potential, -1.06 v or the bromide - bromine potential, -1.087[4].) A plot of indicator current against time of generation (see figure 2) shows a maximum before all the iodide has been oxidized to iodine, and a minimum at the calculated equivalence point. If an equivalent amount of iodine monobromide is prepared as described later, and placed in the titration cell, conditions at the end point of a titration should be approximated. It was found that addition of both iodide and iodate caused the indicator current to increase, supporting the belief that the point of minimum current and the equivalence point are identical.

The point of maximum current can not be used as an exact point of reference in the titration for two reasons: (1) It is not a sharp maximum; (2) Its location does not correspond to the time required to oxidize all iodide to iodine. It can be seen from figure 2 that whereas the endpoint of the titration occurs at approximately 205 seconds, the maximum indicator current occurs at about 70 seconds. When the titration is run in hydrochloric acid with no bromide present (see curve B, figure 2), the maximum is shifted still further, occurring at about 60 seconds.

For these reasons, it was necessary to utilize the point of minimum indicator current in determining the end point. It can be seen from figure 2 that in the vicinity of the endpoint, the indicator current reaches a minimum value, then increases rapidly. If a suitable time after attaining of this minimum current is allowed to elapse (usually two seconds on the high rate, thirty seconds on the low rate), the plot of indicator current is linear and can be safely used for extrapolation.

In an effort to determine the reason for displacement of the current maximum, measurements were made of the solution potential, indicator cathode potential and indicator anode potential against a saturated calomel half cell. These results are tabulated in Table II. Since a fixed potential difference (138 millivolts) is applied across the indicator electrodes, the relative values of E (anode) - E (solution) and E (solution) - E (cathode) indicate the amount of control exercised by that electrode reaction over the diffusion current as a whole. Thus, as the current initially rises, the reactions at the indicator electrodes are:

Cathode: $I_2 + 2e^- = 2I^-$

Anode: $2I^- - 2e^- = I_2$

Here the greatest potential drop is at the cathode, and diffusion of iodine to the cathode controls the magnitude of the diffusion current.

In the region of current maximum (time = 75 sec.), the potential drop is approximately the same at each electrode; diffusion of iodine to the indicator cathode and of iodide to the indicator anode control the magnitude of the diffusion current. At a time sufficient for all iodide to have been oxidized to iodine (time = 104 sec.), the supply of iodide is exhausted, and the electrode reactions become:

Cathode: $I_2 + 2e^- = 2I^-$

Anode: $I_2 + 4Br^- - 2e^- = 2IBr_2^-$

The fact that the greatest potential drop is at the indicator anode indicates that the anode reaction, and hence diffusion of iodine to the anode, controls the magnitude of the diffusion current. Since both anode and cathode reactions involve diffusion of iodine, the indicator current drops off from the maximum.

As the titration proceeds, there is an equilibrium between two reactions at the cathode, bromine being present in equilibrium with the iodine monobromide formed in the titration.

Cathode: $I_2 + 2e^- = 2I^-$

$Br_2 + 2e^- = 2Br^-$

Anode: $I_2 + 4Br^- - 2e^- = 2IBr_2^-$

In the vicinity of the endpoint the concentration of iodine is very small, and the small indicator current can be attributed to the iodine and bromine present in equilibrium with iodine monobromide. There is a sudden shift of potential to the indicator cathode, the electrode reactions becoming:

Cathode: $Br_2 + 2e^- = 2Br^-$

Anode: $2Br^- - 2e^- = Br_2$

After the endpoint, diffusion of bromine to the indicator cathode governs the magnitude of the indicator current.

In figure 2 (curve B.) it can be seen that when iodide is titrated in the absence of bromide, there is little or no indicator current at the end point. This may be explained by the small equilibrium constant for the reaction[4]

$$2ICl\ (aq) = I_2\ (aq) + Cl_2\ (aq) \qquad K = 1.6 \times 10^{-10}$$

as compared with the reaction

$$2IBr\ (aq) = I_2\ (aq) + Br_2\ (aq) \qquad K = 1.2 \times 10^{-5}$$

In an attempt to confirm these conclusions, experiments were made using solutions of iodine in two formal hydrochloric acid. When to such a solution was added a small amount of bromide ion, the indicator current increased only slightly (from 12.8 microamperes to 13.1 microamperes, for example.) But if to such an iodine solution an equal amount of iodide ion were added, the indicator current increased greatly (from 20.0 microamperes to 38.2 microamperes, for example.) The former experiment approximates conditions in the titration when all iodide has been oxidized to iodine; the latter experiment approximates conditions in the vicinity of the point of maximum indicator current.

The small diffusion current which flows at the end point was found to vary with the potential impressed across the indicator electrodes (see figure 3.) When the potential was greater than about 160 millivolts, the indicator current was quite large. By use of an applied potential less than 140 millivolts, this current was kept at a low value (from 0.3 microamperes with a 12 microgram sample to 20 microamperes with a 2000 microgram sample.) At larger values of the applied potential, there is the possibility of an anode reaction involving the oxidation of iodine to higher oxidation states.

The final indicator current was found to be independent of hydrogen ion and bromide concentration, but increased as the quantity of iodide being oxidized increased. In a study of this current, iodine monochloride was prepared by oxidation of iodide with iodate in four formal hydrochloric acid, using the iodine monochloride endpoint[7]. When a sample of this, equivalent to the amount of iodine monobromide present at the end point of a hundred second titration on the high rate, was placed in the titration cell, an indicator current of less than 1 microampere was observed. Upon addition of 5 ml of one formal sodium bromide, the current increased immediately to about 8 microamperes. Titration of an equivalent amount of iodide by electrolytically generated bromine resulted in a final diffusion current of 10 microamperes. The similarity of these values supports the belief that the final diffusion current is caused in part by iodine and bromine in equilibrium with iodine monobromide.

It was found necessary to open the indicator electrode circuit during the course of a titration. In a titration on the high rate, the indicator current was too great to be determined by the microammeter employed. During low rate titrations, the indicator current did not exceed 50 microamperes and hence could be read at all times. However, continual passage of indicator current caused a positive error of several percent in the determination.

The initial indicator current found in all iodide solutions upon acidification is believed to be due to air oxidation. No iodate could be detected in the potassium iodide used. The current was relatively large (5 to 10 microamperes) if stock iodide solutions which had not been treated with carbonate were used. Furthermore, if the iodide samples were acidified and allowed to stand, the initial indicator current increased with time of standing. Small initial indicator currents (1 to 3 microamperes) were obtained by use of iodide solutions 0.005 F to 0.01 F in sodium carbonate; these samples were not acidified until immediately before they were to be titrated. In making calculations, one corrects for the initial indicator current by adding the time equivalent to it, to the observed time of bromine generation.

Attempts were made to titrate iodide in hydrochloric acid solutions in the absence of bromide. This would have the advantage of giving a very small indicator current at the end point. Two difficulties were encountered. Indicator current values were attained very slowly, it being necessary to wait for as long as 30 seconds for a steady value to be reached. Further, it was found that high results were always obtained. In the titration shown in figure 2 (curve B), the calculated time for the end point to be reached (including the correction for the initial indicator current) was 207.4 seconds. The actual endpoint, using the same correction, was 224.2 seconds, a value approximately 8% high. It is believed that this error is due to oxidation of the electrodes in the strong hydrochloric acid solutions used.

<u>Comparison with other micromethods:</u>

Zintl and Betz[8] in aa potentiometric titration with silver nitrate, determined 126 micrograms of iodide with an accuracy of 1%, and 13 micrograms with an accuracy of 4%.

Enders and Kaufmann[1] report a method in which samples containing 1 to 10 micrograms of iodide are oxidized to iodate with bromine water. Upon addition of potassium iodide, iodine is liberated and is distilled off. Treatment of the iodine formed with hydroxylamine results in the formation of nitrous acid, by means of which sulfanilic acid is diazotized. Coupling of the diazonium compound with - napthylamine leads to the formation of a red azo dye, the concentration of which is determined colorimetrically. By this method quantities of iodide from 1 to 10 micrograms are determined with an accuracy of 4%. The complexity of the method, however, excludes it from routine laboratory use.

Kanirath[2] determined small quantities of iodide by oxidizing it to iodate, adding potassium iodide and titrating the liberated iodine with thiosulfate. As in the method of Enders and Kaufmann, six times as much iodide reacts as was originally added. However, this method requires a sample containing 1000 micrograms of iodide.

Laitinen, Jennings and Parks[3] using an amperometric titration with silver nitrate, determined samples containing 635 micrograms with an accuracy from 4% to 13%, and samples containing 254 micrograms with an accuracy of 10% to 11.5%.

In comparison with these methods, the coulometric titration of iodide with electrolytically generated bromine as here described can be conveniently used for routine determination of small amounts of iodide. As Table I shows, samples of iodide as small as 13 micrograms can be determined with an accuracy of ± 2%. In quantities from 65 micrograms to 2000 micrograms, the determination is accurate to ± 0.5%. Titration of a 130 microgram sample takes approximately 200 seconds of low rate generation; titration of a 670 microgram sample takes approximately 100 seconds of high rate generation. The apparatus in its present form can not be used conveniently for the determination of samples containing from 200 to 600 micrograms, and greater than 2000 micrograms because of the excessive time required (greater than 300 seconds.) Provision for an intermediate rate of generation in the apparatus would make possible the determination of samples containing 200 to 600 micrograms of iodide.

Summary:

A coulometric method for the determination of iodide in samples containing from 13 to 2000 micrograms has been developed. Iodide is oxidized by electrolytically generated bromine, the endpoint being determined by an amperometric method. Experiments have shown the method to be accurate to ± 2% for samples from 13 to 50 micrograms, and accurate to ± 0.5% for samples of from 65 to 2000 micrograms. A study of the current flow characteristics of the titration has been made, and an explanation is advanced for the nature of the indicator current.

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TABLE I

Iodide (micrograms)				No. of	
Taken	Found	Error	% Error	Titrations	Av. dev. %
12.8	12.7(a)	-0.1	0.8	5	5.5
25.5	25.8	+0.3	1.2	2	---
38.3	38.7	+0.4	1.0	2	---
64.9	65.2(b)	+0.3	0.46	8	0.93
64.9	65.1	+0.2	0.31	2	---
129.6	130.3	+0.7	0.54	3	0.93
129.6	130.0	+0.4	0.31	2	---
194.5	195.3	+0.8	0.31	2	---
194.5	193.7	-0.8	0.31	2	---
648.4	650.0(c)	+1.6	0.25	6	0.11
648.4	650.5	+2.1	0.32	2	---
669.0	671.5	+2.5	0.37	4	0.15
669.0	672.6	+3.6	0.54	3	0.06
1296.8	1295.3	-1.5	0.12	2	---
1296.8	1299.0	+2.2	0.17	2	---
1338.0	1339.8	+1.8	0.13	2	---
1338.0	1339.4	+1.4	0.10	2	---
1625.6	1622.3	-3.3	0.20	2	---
1625.6	1625.0(d)	-0.6	0.04	4	0.04
2007.0	2008.3	+1.3	0.06	2	---
2007.0	2012.7	+5.7	0.29	2	---

(a) 11.8, 12.1, 12.5, 12.8, 14.2

(b) 64.0, 64.4, 64.6, 65.3, 65.3, 65.6, 65.7, 66.4

(c) 648.4, 649.4, 650.1, 650.1, 650.4, 651.4

(d) 1623.6, 1625.0, 1625.7, 1625.7

TABLE II

Titration of a sample containing 129.6 micrograms of iodide

Time seconds	Current microamperes	E(an.)-E(sol.) millivolts	E(sol.)-E(cat.) millivolts
0	2.0	37	102
40	30.0	36	68
75	39.5	52	42
104	35.5	69	28
140	25.0	91	19
211	4.0	23	112
240	29.5	15	90

Note:

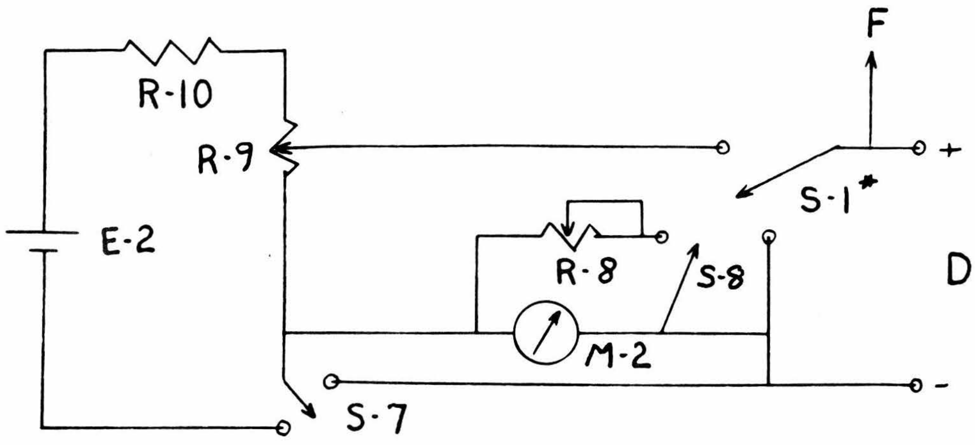
Current = indicator current

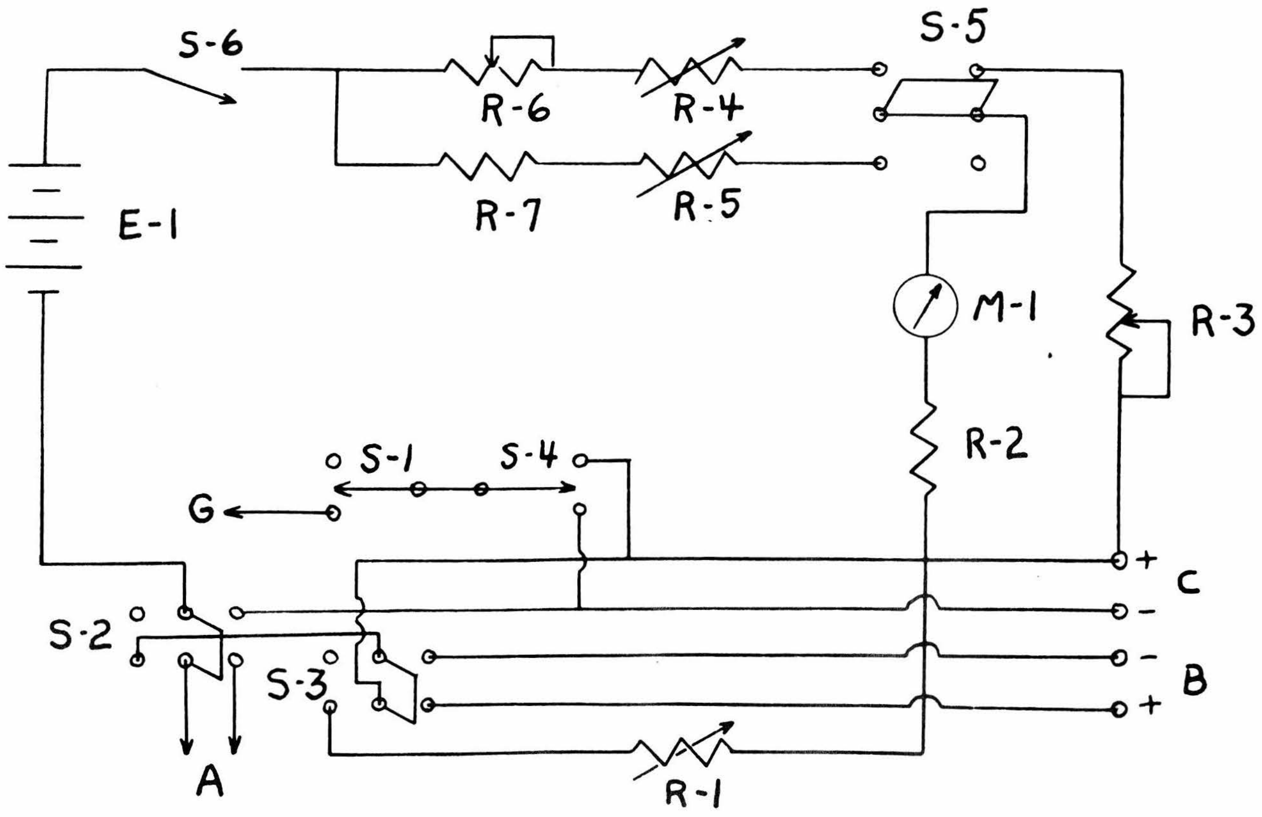
E(an.) = potential of indicator anode against calomel half cell.

E(cat.) = potential of indicator cathode against calomel half cell.

E(sol.) = potential of solution against calomel half cell.

INDICATOR CIRCUIT





GENERATOR CIRCUIT

FIGURE I

SYMBOLS USED IN FIGURE 1

S-1, S-2, S-3, S-5 = DPDT Radio toggle switches

S-4, S-6, S-7, S-8 = SPDT Radio toggle switches

E-1 = Burgess battery #2308 45 v.

E-2 = Burgess battery #4F4 1½ v.

M-1 = Weston meter, model 301 0-1 milliamp.

M-2 = Weston meter, modle 301 0-50 microamp.

A = To electric stopclock

B = To standard resistance

C = To generator electrodes

D = To indicator electrodes

F = To S-1, generator circuit

G = To indicator anode terminal

R-1 = 3,000 ohm wire wound potentiometer

R-2 = 600 ohm, 2 watt carbon resistance

R-3 = 350 ohm, 10 watt semi-variable wire wound resistance

R-4 = 1500 ohm wire wound potentiometer

R-5 = 15,000 ohm wire wound potentiometer

R-6 = 5000 ohm, 10 watt semi-variable wire wound resistance

R-7 = 45,000, 2 watt carbon resistance

R-8 = 2000 ohm, 10 watt semi-variable wire wound resistance

R-9 = 100 ohm, 10 watt semi-variable wire wound resistance

R-10 = 240 ohm, 2 watt carbon resistance

S-1* - S-1 Switches connecting two circuits for electrode treatment

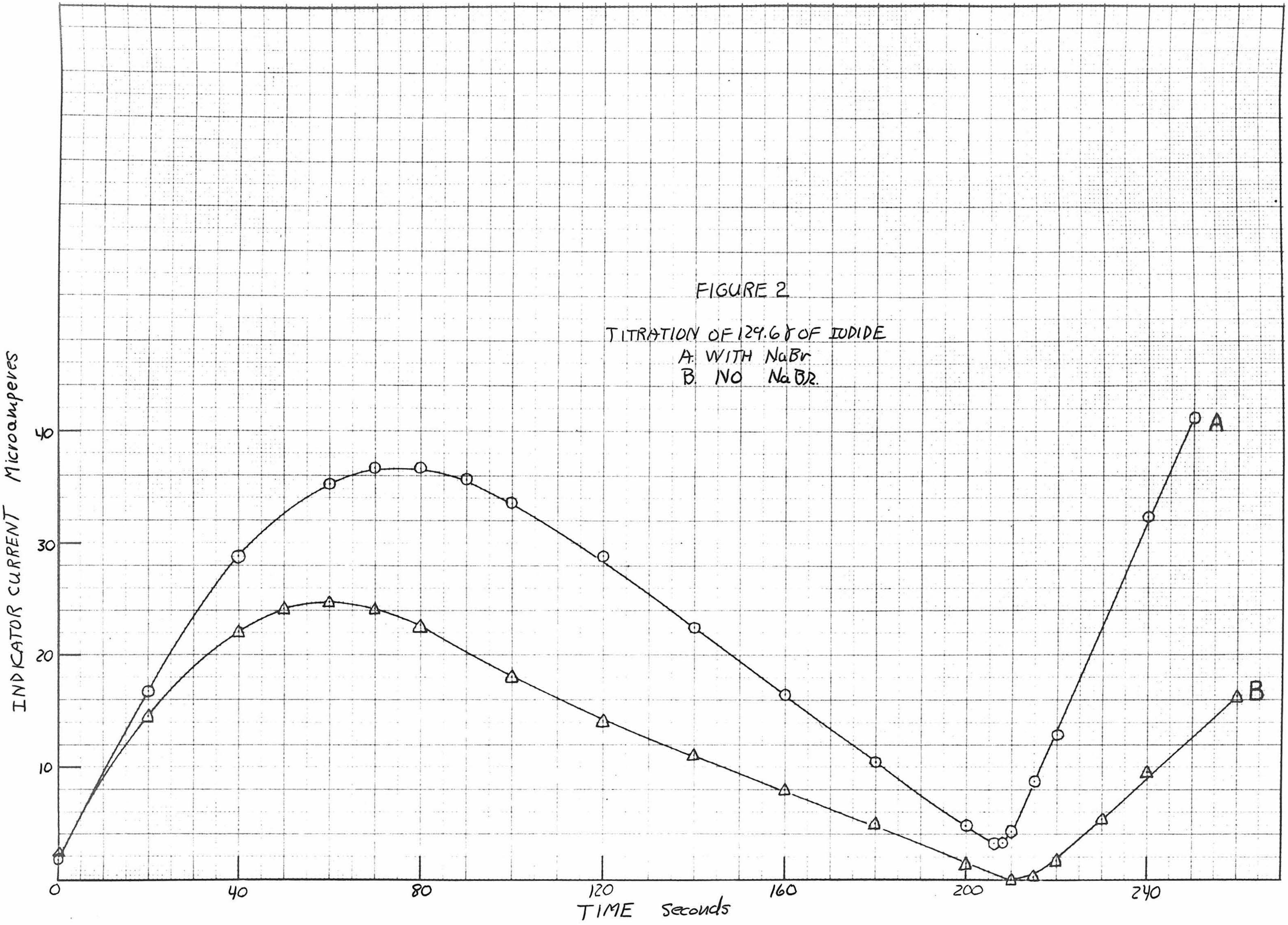


FIGURE 2

TITRATION OF 129.6 γ OF IODIDE
A. WITH NaBr
B. NO NaBr.

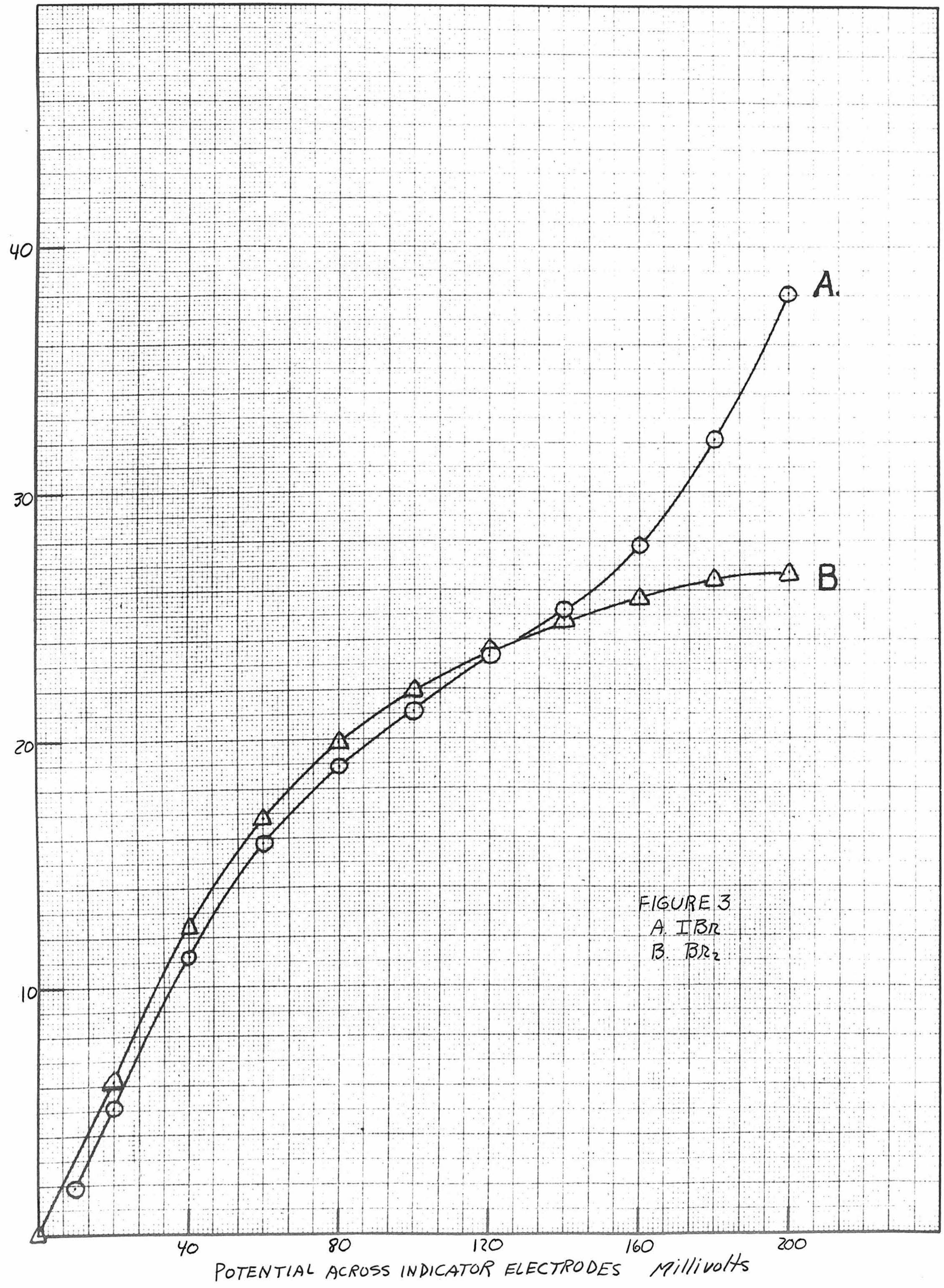


FIGURE 3
A. IBr
B. Br_2