

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY.]

ELECTROMETRIC DETERMINATION OF BROMATE, DICHROMATE, NITRITE AND CHLORIDE IONS.

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The work described in this paper is a continuation of that published in two earlier papers.² The methods and apparatus in this study were in general the same as described in those papers. The aim has been to work out practicable and accurate procedures for the electrometric titration of iodide with the standard and much used oxidizing agents, permanganate, iodate, bromate and dichromate, and to study some of the numerous possible applications. With this paper the first object has been attained, and the method has been applied to the determinations of silver, nitrite and chloride.

Determination of Bromate with Iodide and Permanganate.

To test the accuracy of this determination potassium bromate intended for use as a standard in iodimetry was employed. As received it showed absence of halide when tested with silver, but it was twice recrystallized and dried at 160°. One gram of its solution made by weight should set free 0.006355 g. of iodine from iodide. This value was confirmed by the usual method of titration with thiosulfate solution. One g. of the iodide solution used by electrometric titration was found equivalent to 1.0277 g. of permanganate solution 1 g. of which required 0.003366 g. of sodium oxalate. Numerous series of parallel determinations of iodide solutions by electrometric titrations with permanganate solution and with silver as weighed silver iodide have seemed to prove the sufficiency of the method of standardization with permanganate solution and the gravimetric method has been gradually abandoned. Its results in the case of dilute solutions of iodide where small amounts of silver iodide must be transferred and weighed are not so consistent with themselves in any series as those with the permanganate method. It is evident also that the permanganate method is independent of the presence of small amounts of chloride in the iodide, or any incomplete reduction of the permanganate by iodide as stated by Bray and McKay.³

A known weight of iodide solution was placed in the titration vessel, sufficient 10 *N* sulfuric acid was added to make the whole solution about

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² Hendrixson, *THIS JOURNAL*, **43**, 14, 858 (1921).

³ Bray and McKay, *ibid.*, **32**, 1193 (1910).

2 *N* at the end of the experiment, the stirrer was started and bromate solution was added in amount to leave at least 10% of the iodide undecomposed. The voltage became constant in a few moments and the titration was then completed with permanganate solution. Since chlorate might occur in either bromate or permanganate, even though experiments of my own indicated that it would have no influence, volumes of pure 0.05 *N* chlorate solution about equal to the bromate were added in Expts. 5 to 7 in the following table. In this table the weights of iodide are those used less the equivalent weights of the permanganate used to titrate the excess of iodide. In all the tables weights of substances, theoretical and found, are for 100 g. of solution.

TABLE I.—TITRATION OF BROMATE WITH IODIDE AND PERMANGANATE.

Expt.	KBrO ₃ G.	KI. G.	Iodine calc.	Iodine found.	Deviation.
1.....	26.69	25.86	0.6355	0.6351	—4
2.....	42.03	40.73	0.6351	—4
3.....	31.46	30.48	0.6350	—5
4.....	27.93	27.05	0.6347	—8
5.....	30.38	29.43	0.6348	—7
6.....	27.78	26.93	0.6353	—2
7.....	27.63	26.77	0.6349	—6
Average					—5.1

Direct Titration of Iodide Solution with Bromate Solution.

Hydriodic acid can be titrated directly with bromate solution in the presence of at least 2 *N* sulfuric acid. The same solutions of bromate and iodide used in the determinations of Table I were used in those of Table II. In order to know the voltage at the end-point in using weighing burets a titration with pipet and buret was made and Curve 1 of Fig. 1 was plotted. It may be observed that the curve shows almost as large and abrupt a rise in voltage as the permanganate and iodate curves, Nos. 3, 4, 5 of Fig. 1 in an earlier paper.¹ The deliveries of the pipet and buret were weighed and the curve found to correspond with the known

TABLE II.—TITRATION OF IODIDE WITH BROMATE IN 2 *N* SULFURIC ACID.

Expt.	KBrO ₃ G.	KI. G.	Iodine calc.	Iodine found.	Deviation.
1.....	25.62	24.86	0.6355	0.6361	+6
2.....	37.60	36.44	0.6351	—4
3.....	43.44	42.11	0.6352	—3
4.....	43.13	41.81	0.6353	—2
5.....	49.14	47.74	0.6366	+11
6.....	56.87	55.13	0.6353	—2
Average					+1

¹ THIS JOURNAL, 43, 860 (1921).

concentrations of the solutions. The last drops of the bromate solution must be added very slowly to avoid running by the end-point which was assumed at 0.53 volt. The titration requires at least 15 minutes merely to attain the correct end-point and much longer to titrate for such a curve. The results are very concordant. Six titrations were made and all are included in the table on opposite page.

In one of his recent papers the writer has discussed the effect of the presence of hydrochloric acid in the titration of the iodide solution with permanganate and iodate solutions in sulfuric acid as the main acid medium and titration with iodate in hydrochloric acid alone, and reached the conclusion that when present in excess of 0.2 *N* hydrochloric acid no longer afforded curves from which end-points could be accurately determined. The harmful influence of this acid is much greater in the titration of iodide with bromate, and greater still when

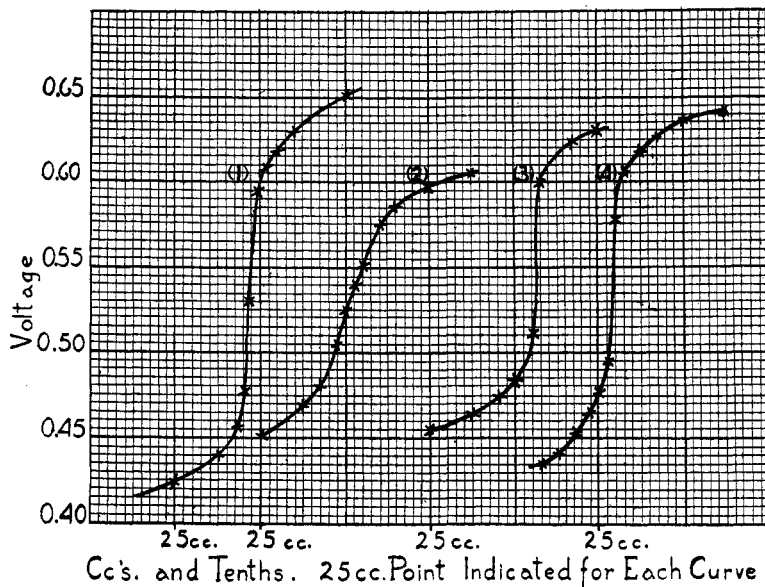


Fig. 1.

dichromate is used as the oxidizing substance. One reason is clear. The bromate and dichromate require the presence of such a large amount of acid, that in case it is hydrochloric its effect is to prevent an abrupt rise in voltage where the end-point should be thus indicated and so to render the curve worthless. Many titrations with bromate solution were made in hydrochloric acid from 0.2 *N* to 1 *N*. Curve 3, Fig. 1, is the best obtained from several titrations in 0.2 *N* hydrochloric acid. The form is good, but as a matter of fact at the end-point indicated, a known excess

of 0.35 cc. of bromate solution had been added to the iodide. The other curves varied from this amount to about 0.6 cc. excess. Several titrations in 0.5 *N* hydrochloric acid were made, and Curve 2, Fig. 1, shows the best result, which so far as one may judge shows an end-point about 0.1 cc. in excess. More concentrated acid produced curves approximating straight lines with inclinations nearer the abscissa. The same effect is shown in the titrations carried out by I. M. Kolthoff¹ when one plots his results to the same scale as used here in Fig. 1. His best curve thus drawn closely approximates Curve 2, Fig. 1.

The difficulties met in the direct titration of iodide with bromate in hydrochloric acid seem to become insuperable when one attempts to titrate with dichromate. Apparently more acid is required. In another connection, the titration of dichromate with an excess of iodide and thiosulfate in the ordinary way, Kolthoff² emphasizes the need of 30 cc. of 4 *N* hydrochloric acid in 100 cc. if the thiosulfate is to be added within a few moments, and 15 cc. if one adds it after 5 minutes. Certainly as much would be required in electrometric titration where iodide and dichromate are supposed to destroy each other completely at the end-point, and such an amount seems to be inconsistent with the abrupt rise in voltage. The writer made many titrations in hydrochloric acid solution from 0.2 *N* to 2 *N* and in all cases the plotted curves were worthless, and did not differ greatly from straight lines. The following is a fair illustration showing the titration of 25 cc. of iodide solution with dichromate solution, each almost exactly 0.05 *N*, with 20 cc. of 4 *N* acid, and the total volume 100 cc.

Dichromate, cc.	24.0,	24.5,	25.0,	25.5,	26.0,	26.5,	27.5
Voltage	0.436,	0.442,	0.460,	0.478,	0.496,	0.504,	0.514
Differences		6	18	18	18	8	10

The voltage was only 0.514 with an excess of 10% of chromate. At this point 20 cc. more of 4 *N* acid was added and the voltage fell to 0.494. It therefore, seems clearly impossible to titrate iodide with dichromate in hydrochloric acid solution by the electrometric method. In fact this acid lowers the voltage and obscures the end-points when iodide in its presence is titrated with any of the oxidizing agents used in this study. It is hoped to carry out determinations of other reducing agents, where iodine would not be involved, with chromate and other oxidizing agents. It is possible that the difficulty discussed might be due to the well-known fact that hydrochloric acid itself at no great concentration reduces any of these oxidizing substances and it is possible that many side reactions might occur to a disturbing extent when the iodide concentration has become very small near the end-point. Chlorine set free might escape

¹Kolthoff, *Rec. trav. chim.*, **39**, 211 (1920).

²Kolthoff, *Z. anal. Chem.*, **59**, 401 (1920).

or form hypochlorous acid, or it might attack the free iodine forming iodic acid or iodine chloride. It seems to the writer at present that both experiment and theory require the use of sulfuric acid in such electrometric titrations instead of hydrochloric, since in dilute solutions sulfuric acid is quite indifferent toward both oxidizing and reducing agents.

Direct Titration of Iodide with Dichromate.

Some time ago the writer titrated dichromate indirectly by adding its solution to an excess of iodide solution and dil. sulfuric acid, and determining the excess of iodide with permanganate solution, thus securing very accurate results.¹

Iodide may also be titrated directly with dichromate in sulfuric acid solution of at least 2 *N* concentration, if sufficient time is allowed near the end-point for the reaction to reach completion. The dichromate must be added very cautiously and at least half an hour is required to reach without passing the end-point. To determine the voltage at which the end-point should be taken when titrating by weight, a preliminary titration with an ordinary buret and pipet was made which is represented by Curve 4, Fig. 1. It required an hour; probably this time was not sufficient, since the curve shows apparently about 0.1 % excess of dichromate solution. It may in fact be said that after adding dichromate solution near the end-point the mirror reflection of the highly sensitive galvanometer never became quite stationary, but continued to drift in the direction of higher voltage. Hence it is probable that a very high degree of accuracy of the end-points taken in the experiments of Table III cannot be justly claimed, even though the results agree practically with theory. The potassium dichromate used was Kahlbaum's, four times recrystallized and dried at 180°. One g. of the solution made by weight should set free 0.006356 g. of iodine from potassium iodide. The ratio of the iodide by electrometric titration was one g. to 0.999 g. permanganate, one g. of which required 0.003366 g. of sodium oxalate.

TABLE III.—DIRECT TITRATION OF IODIDE WITH DICHROMATE.

Expt.	K ₂ Cr ₂ O ₇ . G.	KI. G.	Iodine calc.	Iodine found.	Deviation.
1.....	34.73	34.62	0.6356	0.6351	—5
2.....	32.64	32.55	0.6353	—3
3.....	44.18	44.07	0.6355	—1
4.....	32.29	32.24	0.6361	+5
5.....	40.91	40.81	0.6355	—1
				Average	—1

¹ Hendrixson, *THIS JOURNAL*, 43, 14 (1921).

So far as experience extends the direct titration of iodide in sulfuric acid solution with dichromate will give consistent and accurate results if one allows sufficient time for the reaction to complete itself, but one can save time by using the indirect method ending with permanganate as already explained.

Determination of Nitrous Acid.

The best methods for the determination of nitrous acid and nitrites seem to be those depending upon the oxidation of the nitrite to nitrate by running the nitrite solution into an excess of permanganate solution, and determining that excess with a reducing agent. Raschig¹ recommends running the nitrite into an excess of neutral permanganate solution, adding an excess of acid, then an excess of iodide and titrating the liberated iodine with thiosulfate solution. Laird and Simpson² run the nitrite into an excess of permanganate solution acidified with sulfuric acid, then add an excess of ferrous iron, sodium oxalate or hydrogen peroxide, and complete the titration with permanganate. They offer objection to Raschig's method on the basis of the work of Bray and McKay³ who assert that permanganate standardized with sodium oxalate sets free from iodide slightly less than the theoretical amount of iodine as determined with thiosulfate standardized with pure iodine, and believe this difference to be due to the incomplete reduction of permanganate by hydriodic acid. It seemed to the writer that such objection might be removed and any possible error from this source be eliminated by destroying the excess of permanganate with an iodide solution which had also been standardized with sodium oxalate solution through the medium of the same permanganate and finally titrating the excess of iodide with the permanganate electrometrically. This would avoid also any error that might result from the presence of iodate in the iodide, or from the vaporization of iodine in the method of Raschig.

It seems impracticable to prepare a nitrite pure and stable enough to give its theoretical value in solution, thus serving as the basis for testing a new method. It seemed better to carry out in parallel experiments the determination of an arbitrary solution of the best analyzed potassium nitrite both by the method of electrometric titration, and by that of Laird and Simpson⁴ which seems theoretically the best. Its authors have supported the accuracy of the latter method by the determination of a nitrite solution, which they had standardized by reducing with it silver

¹ Raschig, *Ber.*, **38**, 3911 (1905).

² Laird and Simpson, *THIS JOURNAL*, **41**, 524 (1919).

³ *Loc. cit.*

⁴ *Loc. cit.*

bromate and weighing the silver bromide according to the method of Busvold.¹

In carrying out the method of Laird and Simpson the writer used sodium oxalate as the reducing agent to avoid errors due to the instability of ferrous iron and peroxide solutions. In every instance hydrated manganese dioxide was precipitated at the point of disappearance of the permanganate color, but readily dissolved on adding a small excess of oxalate. By this method five determinations gave for 100 g. of the nitrite solution, 0.5437, 0.5438, 0.5443, 0.5443, 0.5434 g. of nitrous acid. The greatest variations from the mean, which is 0.5439, are +0.0004 and -0.0005 g.

In carrying out the method of Laird and Simpson the oxalate solution used was made to contain in one g. 0.00335 g. of sodium oxalate. With it was standardized the permanganate solution, one gram of which was equivalent to 1.0007 g. of oxalate solution. The ratio of the permanganate to the iodide solution used in the method by electrometric titration was 1 to 1.1716 g.

In carrying out the electrometric method weighed permanganate solution was run into the titration vessel, diluted and 10 *N* sulfuric acid was added in sufficient quantity to make the final solution about 1.5 *N*. The mechanical stirrer was started and the nitrite solution slowly added in amount to leave 5 to 10% of the permanganate unchanged. After about 5 minutes an excess of iodide solution was added and the titration was completed with permanganate solution. In the dilute solution the iodine set free did not precipitate, and observation failed to detect manganese dioxide at any stage. Special experiments with very dilute solutions failed to show any oxide.

TABLE IV.—DETERMINATION OF NITRITE BY ELECTROMETRIC TITRATION.

Expt.	NaNO ₂ . G.	KMnO ₄ . G.	HNO ₂ found.	Deviation.
1.....	36.41	56.48	0.5445	+6
2.....	37.21	57.61	0.5436	-3
3.....	43.06	66.69	0.5435	-4
4.....	37.83	58.63	0.5440	+1
5.....	37.36	57.86	0.5436	-3
6.....	42.79	66.33	0.5441	+3
		Average	0.5439	

It is by chance of course that the average result is again 0.5439 and the deviations +0.0006 and -0.0004, but due allowance being made for chance the evidence that both methods are essentially accurate is very strong.

¹Busvold, *Chem.-Ztg.*, **38**, 28 (1914).

Attention is called to the fact that it is not necessary to end the titration with permanganate, though it is time saving and just as convenient since one has at hand his weighed buret of permanganate. Preliminary experiments showed that titrations made with permanganate and iodide solutions alone carried out by running permanganate solution into the iodide solution agreed within one part in 1000 with those in which the iodide was run into the permanganate solution if one gave sufficient time for the reduction of the iodic acid always formed when iodide is added to an excess of acidified permanganate. Expt. 6 of Table IV was completed by running iodide into the excess of permanganate solution to the end-point.

Determination of Chlorine.

In a former paper¹ the determination of silver by indirect electrometric titration was described. As one might infer, another step leads to the determination of the chlorine ion. It requires a known solution of silver and of course solutions of iodide and permanganate. To test the method an approximately 0.05 *N* sodium chloride solution was made. Its concentration was determined with silver, weighed as silver chloride, and one g. was found to contain 0.0017837 g. of chlorine. A known solution of silver was made from the same lot of pure silver previously described.² In carrying out the method, the weighed chloride solution was subjected to the stirrer and an excess of silver added. When the precipitate was coagulated and settled completely the solution was filtered through asbestos in a Gooch crucible and into the titration vessel. Filtering is necessary in case of the silver chloride. Otherwise it would be largely changed later to iodide. To the perfectly clear filtrate was added the necessary sulfuric acid, and a small excess of iodide solution of known concentration and this excess was titrated in the usual way with permanganate solution. As previously stated the insoluble silver iodide does not interfere. The following are the results of all of the determinations, expressing the weights of chlorine in 100 g. of the sodium chloride solution:

0.17835, 0.17845, 0.17815, 0.17852, 0.17862, 0.17822, 0.17834.

The mean is 0.17838, and the greatest deviation +0.00024 and -0.00023, or about 1 part in 750.

The method may seem involved and probably would be for single determinations of chlorine, but might prove very useful in routine work, if burets and pipets of suitable capacities were used. It requires filtration, but this is also true of the only other volumetric method for

¹ Hendrixson, *THIS JOURNAL*, 43, 863 (1921).

² *Loc. cit.*

the chlorine ion which is generally applicable to large and small quantities of chlorine in acids solution. Of course the method should serve equally well for bromide ion.

Summary.

1. In this paper is described the direct electrometric titration of iodide with bromate and dichromate, and the indirect titration of bromate with the aid of permanganate; also the determination of nitrite and chloride ion.

2. The direct titration of iodide with bromate or dichromate can be done accurately in at least 2 *N* sulfuric acid solution, but much time is required to reach the true end-points, and the indirect titration, ending with permanganate, is preferred.

3. In earlier work titration of iodide with permanganate or iodate in hydrochloric acid solution was found impracticable. Accurate titration of bromate or dichromate in this medium is found impossible.

4. The method for nitrite requires solutions of known concentration of iodide and permanganate, both essentially permanent and both determinable by reference to the same standard, namely, sodium oxalate. The method eliminates error from supposed incomplete reduction of permanganate by hydriodic acid, or from the presence of any chloride or iodate in potassium iodide.

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NOTES.

A Rapid Method for Determining the Density of Air.—This method depends upon the measurement of the buoyant effect of the air upon an object of considerable volume.¹ A sealed globe of known exterior volume is weighed under accurately known conditions of temperature, pressure and humidity. From the conditions, the density of the atmosphere at the time of weighing and the buoyant effect of the air upon the globe and weights are computed. By adding the difference between the buoyant effect on the globe and on the weights to the weight of the globe in air, the weight of the globe in vacuum is found.

If the globe is weighed in the air under any conditions, the weight of air displaced by the globe in excess of that displaced by the weights is readily found by subtraction from the weight in vacuum. This difference divided by the volume of the globe less the volume of the weights yields the atmospheric density; or the desired result may be more conveniently read from a graph in which the apparent weight of the globe is plotted against atmospheric density.

¹ The buoyancy method of determining gas density has frequently been applied. See, for example, Jacqueroed and Tourbaian, *J. chim. phys.*, **11**, 3, 269 (1913); Edwards, Bur. of Standards, *Tech. Paper*, **89** (1917).