

If the devitrification of glass were dependent upon the formation of crystal nuclei upon the surface or within the mass of the glass, a cool storage space would seem to be ideal; my experience has, however, been that glass which had been stored in an attic room under a slate roof for 15 years showed less tendency to devitrify than another lot stored in a ground floor room of our reinforced concrete laboratory for 5 years. This is perplexing unless we admit that devitrification depends upon absorption of moisture; the atmosphere of the laboratory has an average humidity much higher than the atmosphere of the attic room, which is in another building. Certain gases present in the atmosphere of a chemical laboratory also seem to play a part, probably acting catalytically; halogen gases, except those containing fluorine, for obvious reasons, seem especially active in this way. A tube which had contained phosgene devitrified badly before the blowpipe; the same tube, after having been exposed casually to the laboratory fumes for more than 6 months, no longer showed any tendency to devitrify.

Summary.

That the devitrification of glass before the flame is a surface phenomenon is shown by the fact that the tendency to devitrify may be removed by rinsing the parts to be fused with dil. hydrofluoric acid, thus removing the surface. Old apparatus which has been broken may be repaired by taking advantage of this fact.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF GRINNELL COLLEGE.]

THE ELECTRO-TITRATION OF HYDRIODIC ACID AND ITS USE AS A STANDARD IN OXIDIMETRY.

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The determination of the iodine ion when not associated with chloride or bromide is simple and accurate, gravimetrically as silver iodide, volumetrically by the Volhard method; but, when mixed with either of the other halogens or both, as it is likely to be, its determination is difficult and this has formed one of the perennial problems of analytical chemistry for nearly a century. The literature contains, of course, a large number of varieties of methods for the volumetric determination of iodides, but they can be reduced to a few clearly marked types. Special citations here seem unnecessary since the whole subject is being worked out, reviewed and criticised by I. M. Kolthoff,¹ under the general title "Iodometric Studies."

¹ Kolthoff, *Pharm. Weekblad*, **56**, 391, 572, 878, 1322, 1466 (1919); **57**, 53, 82 (1920); cf. *Chem. Abst.*, **13**, 1434, 1569, 3103 (1919); **14**, 34, 504, 1270, 1271 (1920).

A study of these methods and the criticisms indicates that none is accepted as entirely satisfactory. It occurred to the writer that it might be possible to attack successfully this old problem with the comparatively new process of electro-titration, using an oxidizing agent that could be accurately standardized, one sufficiently stable and yet sensitive enough to react completely with hydriodic acid when both are present in equivalent weights, and at room temperature. The problem would then be merely one of finding the end-point by the sudden rise of potential when the oxidizing agent was added in amount to complete the reaction. Iodine would not have to be determined at all; thiosulfate with its instability and possible side reactions would not be used. So far as this study has been carried, potassium permanganate seems to meet these requirements as the data to be submitted indicate.

Apparatus.

Preliminary experiments were made with a Leeds and Northrup potentiometer and it was used from time to time for comparison. Some of the analyses of this paper were made with it. It was soon realized, however, that measuring the exact rise of potential was unimportant, the essentials being the position and sharpness of the rise, with reference to the permanganate added.

Using this potentiometer with its 2 shifts made the work undesirably slow and recourse was taken to the idea of Roberts, and Roberts and Hostetter,¹ and with such satisfactory results that the instrument as improved seems to merit some description. Roberts attached a 30 cm. ruler parallel to the slide beam of a common form of rheostat of about the same length, which enabled him to read the changes in voltage in millimeters, thus converting his variable resistance into a potentiometer, crude but sufficient for his purpose, and dispensing with the separate voltmeter used in several forms of titration apparatus, and the need of readjustment when it is put in circuit. The writer selected a rheostat having a coil 425 mm. long, made of about 650 turns of oxidized resistance wire, closely contact wound, and having a resistance of 169.45 ohms. The polished square brass beam carrying the slide contact was accurately graduated in mm. by a local tool company, and the contact points were narrowed so as to touch only 2 wires at the same time.

Since the voltage of the titration cell never exceeds about 0.8 in these measurements, the calculated resistance, 229 ohms, was added by means of a box to the end of the instrument not traversed by the contact slide. This makes the scale in effect one meter long and the value of one mm. equals 2 millivolts, approximately, when one storage cell is used as a balance. The potentiometer without the extension was calibrated to every 5 cm. The results combined with measurements of known voltages with it,

¹ THIS JOURNAL, 41, 1337, 1359 (1919).

indicate that its error nowhere exceeds 0.4%, is smaller in the region of measurement, and smaller yet when used with its virtual 1500 turns of wire.

A damped movable coil galvanometer with rated sensitiveness 106 megohms was used, and was none too sensitive. With it was used the Leeds and Northrup electric lamp and etched scale. The titration vessel was a 3-neck Woulff bottle with a hole bored for the tip of the buret. One neck held the drawn-out tube for the washed carbon dioxide or compressed air by which the solution was vigorously stirred. The others held the usual form of calomel electrode with a normal solution of potassium chloride and the small bright platinum electrode. All volumetric vessels were made after Bureau of Standards designs and graduated for 20°. They were calibrated. Measuring by delivery from flasks was avoided where possible. In the few cases when necessary to measure out water, corrections were made by weighing the adherent water. In all the titrations after those of the first series only weighing burets were used.

Titration of Hydriodic Acid with Permanganate.

To test the new method it was necessary to prepare an iodide practically free from other halogens so that its solution could be standardized with silver. To make potassium iodide pure enough for the purpose, about 220 g. of "Analyzed" iodine was ground with about $\frac{1}{3}$ its weight of "Special" potassium iodide and sublimed slowly in a Pyrex beaker, a flask fitting the beaker and containing cold water serving as the condenser. The iodine was then sublimed alone. It was converted into phosphorous iodide with washed red phosphorus, and this was hydrolyzed with the minimum of water. The gas was passed over dry red phosphorus and absorbed in water. For the determinations in the first series this solution was made slightly alkaline with potassium carbonate, testing free from halogens and this solution was used directly. For all subsequent work a solution prepared in the same way was evaporated, the iodide was fractionally crystallized out, and only the first fraction was used. A part of the first iodide solution prepared 8 months ago yet remains water clear, and shows no color on acidifying. This solution was diluted and its concentration determined gravimetrically with silver, which gave one cc. equivalent to 0.002819 HI, approximately 0.02 *N* strength.

The solution of permanganate was standardized with sodium oxalate supplied by the Bureau of Standards, which had been dried at 145°. Several closely agreeing analyses gave one cc. equal to 0.001328 g. of sodium oxalate, which is equivalent to 0.002536 HI or 0.02 *N* \times 0.991.

In the titrations of the first series 20 cc. of iodide solution was added to the titration vessel from a pipet, 125 cc. of water and enough diluted sulfuric acid to make the volume at the end of the titration about 200 cc. and the acidity about normal. The air or carbon dioxide was started, and the permanganate added from a buret, rapidly at first, in portions

of 0.5 to 0.1 cc. near the end-point. The curve was plotted and the end-point taken at the middle of the nearly vertical rise of about 80 mm. on the scale, or 0.16 volt.

Approximately 0.02 *N* solutions have been adhered to, though many experiments with 0.01, 0.05 and 0.1 *N* solutions indicated a wide range of choice in this respect.

Series I.—Nine determinations with solutions as just described gave the average content of hydriodic acid in 20 cc. of potassium iodide as 0.05639 g. while several determinations as silver iodide gave 0.05638 g. The greatest deviations from the latter in the titrations were -0.00009 and $+0.00016$ g.

To the titration vessel in 2 of these determinations were added, respectively, 10 cc. and 20 cc. of 0.1 *N* hydrochloric acid without causing a difference in the results, though the abrupt rise in voltage was not so great.

Four additional experiments were made with the same solutions, but with the addition of the volumes of 0.02 *N* potassium bromide solution given below to determine its degree of interference.

Volumes 0.02 <i>N</i> KBr, cc.	2	5	25	50
Hydriodic acid found.....	0.05639	0.05654	0.05666	0.05679

It seems, therefore, that chloride will not interfere with the determination of iodide by this method even when its amount exceeds that of the iodide several times. In the case of bromide amounts exceeding 25% of the iodide gave high results. The voltage rise becomes progressively less abrupt and the true end-point more uncertain. Neither of these halogens is likely to interfere when present in moderate quantities as impurities in iodides.

The influence of nitric acid was also studied. It was freed as far as possible from nitrous acid by fractioning after suitable dilution, and used as soon as possible. Apparently its interference when thus freshly purified is very small, up to 2 *N* concentration in the titrating vessel; and any interference is due to the inevitable small amounts of nitrous acid. The subject of interference will receive further attention.

The accuracy of the electro-titration of iodide was further tested in the preparation of known solutions of iodide to be used in the electro-titration of potassium dichromate to be described later. In this and all subsequent work only weighing burets were used, thus avoiding errors due to change of temperature, want of uniformity in drainage of burets and pipets, and permitting the use of larger masses of solutions. Though not necessary to change weights to volumes, the change has been made to avoid confusion likely to arise from the use of data on two bases in the same paper. To calculate weights to volumes the densities of all solutions were accurately determined.

Series II.—Several determinations of a new solution of potassium

iodide with silver gave the concentration $1.0033 \times 0.02 N$. The same solution was titrated with newly standardized permanganate and showed concentration $1.0022 \times 0.02 N$.

Series III.—A third solution of iodide showing concentration $0.9942 \times 0.02 N$ as determined with silver gave $0.9937 \times 0.02 N$, when titrated electrometrically with a third solution of permanganate.

Therefore, a score of determinations in 3 wholly different series seems to show that hydriodic acid may be accurately titrated with permanganate. In Series II and III, the normality of the iodide solution appears about one part in 1000 in II and one part in 2000 in III smaller when determined with permanganate. The former is about the limit of accuracy even when titrations are made by weight. These differences may be accounted for by the fact that under suitable conditions the galvanometer marks the true end-point while the eye requires a certain excess of permanganate in standardizing permanganates with oxalate.

If these results are valid it is obvious that either known permanganate or known iodide may be used to standardize the other. Even ordinary potassium iodide may be standardized with permanganate regardless of small amounts of other halides as they are likely to occur. On the other hand, known pure iodide solution as determined gravimetrically with silver should be an accurate and ever ready means of standardizing permanganate by this method.

It seemed evident that with certain modifications this method might be used to standardize dichromate and iodate, and what is of no less interest, it should offer a wholly new line of approach to the old problem of the super-oxidizing power of potassium dichromate first asserted by Julius Wagner¹ in the equivalent of these words: "Practically the conclusion is that one must throw aside potassium dichromate as a means of iodometric standardization." He found the amount of iodine set free on the average 0.3% too high, and ascribed the excess to a catalytic agent accelerating the action of the oxygen of the air on hydriodic acid. Quite recently Bruhns,² in a similar study, failed to confirm the results of Wagner, either in the amount of the excess or its reduction by exclusion of air and stirring with carbon dioxide. In fact when the present atomic weight of chromium is used, practically theoretical results are obtained. On recalculating Wagner's data, using 52 instead of 52.14, the value assigned at that time, $\frac{1}{3}$ of the average excess found by him disappears. Both Bruhns and Kolthoff³ are inclined to attribute variations from theory as largely due to unsuitable concentrations of acid, and secondary reac-

¹ J. Wagner, *Z. anorg. Chem.*, **19**, 427 (1899).

² Bruhns, *J. prakt. Chem.*, **93**, 73, 312 (1915); **95**, 37 (1917); *C. A.*, **10**, 2857 (1916); **11**, 2758 (1917).

³ *Loc. cit.*

tions under these conditions. Still more recently McCrosky¹ made a study of this question and found that some samples of dichromate have high oxidation values; that the removal of air acts as a corrective; that the excess may be due to an impurity in the dichromate which is not removable by recrystallization.

Titration of Potassium Dichromate.

In attacking this problem it was evident that unusual precaution must be taken. The water and acid used were tested from time to time, and gave a rise of about 0.26 volt for one drop of a 0.05 *N* solution of permanganate. The usual acidified solution of potassium iodide was agitated by a stream of air as purified, and portions were tested with starch from time to time. In 20 minutes starch showed free iodine; in half an hour free iodine was evident by its own color. Since the actual titration requires not more than 10 minutes, error from this source seems excluded.

With weighing burets the determination of the end-point by plotting is impracticable, but many plotted curves had shown that the end-point could be taken without sensible error between 0.58 and 0.62 volt, and it was taken as nearly as possible at 0.60. The solutions used for titration of dichromate standardized as under Series II were protected by opaque housings.

The first sample of dichromate used was prepared from a quantity of the salt imported from Kahlbaum many years ago which was recrystallized 4 times. After the first filtration it was not in contact with filter paper and was carefully protected from dust. It was finely powdered and heated several hours at 185°. Of this salt 1.9614 g. was dissolved and the solution made up at 20° to 2000.2 cc. Its density was 1.00095. Apparently hydriodic acid can be titrated directly against neither dichromate nor iodate by running their solutions into hydriodic acid to the end-point. There is no such abrupt rise in potential as in the case of permanganate, and the position of the end-point is not so evident. The titration can be accurately made by adding chromate to an excess of iodide and titrating the excess with permanganate.

In the titration of dichromate the current of air or carbon dioxide was started and there were added in succession about 50 g. of iodide solution, 25 g. of chromate, 75 cc. of water and 25 cc. of 8 *N* sulfuric acid. After the voltage had become stationary, the necessary permanganate was added till 0.6 volt was indicated. For ready comparison it seems best to give in Tables I-IV the weights as they would be if all solutions were exactly 0.02 *N* and of unit density. The weights of the iodide are unchanged, since its density and normality are both represented by 1.0028. The weight of chromate was divided by 1.001; the permanganate divided by 1.0007 and multiplied by the factor 0.9891. The weights have hence

¹ McCrosky, *THIS JOURNAL*, 40, 1662 (1918).

the same relation as volumes of the same normality and correspond closely to Mohr cc., not having been reduced to vacuum and 4° standard.

TABLE I.

Titration of Dichromate with Hydriodic Acid. Air Stirring. Kahlbaum's Pure Potassium Chromate, 4 Times Recrystallized.

Expt.	0.02 N KI. Cc.	0.02 N KMnO ₄ . Cc.	KI used by chromate. Cc.	Chromate present. Cc.	Deviation KI used. Cc.
1.....	50.074	25.172	24.902	24.926	-0.024
2.....	50.126	25.102	25.024	25.030	-0.006
3.....	50.157	25.377	24.780	24.781	-0.001
4.....	50.103	25.253	24.850	24.848	+0.002

Av., -0.007

It may be noted that with air stirring, and assuming that the iodide and permanganate destroy each other in exact equivalents, the volumes of the iodide and chromate equal each other within one part to about 3600, which is beyond the limit of accuracy in titration.

The experiments represented in Table II were carried out in precisely the same way except that carbon dioxide was used for stirring, and the well-washed gas was allowed to flow several minutes before the sulfuric acid and permanganate were added. The gas was generated in a Kipp's apparatus, that run off from a cylinder of liquid carbon dioxide being found for some reason quite unfit for use.

TABLE II.

Titration of Dichromate with Hydriodic Acid. Carbon Dioxide Stirring. Kahlbaum's Potassium Dichromate 4 Times Recrystallized.

Expt.	0.02 N KI. Cc.	0.02 N KMnO ₄ . Cc.	KI used by chromate. Cc.	Chromate present. Cc.	Deviations KI used. Cc.
1.....	49.802	24.535	25.266	25.253	+0.013
2.....	50.412	25.491	24.921	24.950	-0.029
3.....	50.237	25.303	24.934	24.955	-0.021
4.....	49.897	24.050	25.847	25.860	-0.013

Av., -0.012

Here again, granting that the standardizations of the iodide and permanganate were correct, the iodide used its own volume of chromate within about one part in 2100, which is again beyond the limit of accuracy. It is to be noted that there is a difference in the results with air stirring and stirring with an indifferent gas of only one part in 5000.

A sample of Baker and Co.'s analyzed potassium dichromate was next 3 times recrystallized, powdered, dried at 185°. Of this preparation 0.9806 g. was weighed and dissolved, and the solution made up to 1000 cc. in a calibrated flask at 20°. Precisely the same method of titration was used as described above (Table I).

TABLE III.

Titration against Hydriodic Acid of Baker's Potassium Dichromate 3 Times Recrystallized. Air Stirring.

Expt.	0.02 N KI. Cc.	0.02 N KMnO ₄ . Cc.	KI used by chromate. Cc.	Chromate present. Cc.	Deviation KI used. Cc.
1.....	49.720	24.723	24.997	25.020	-0.023
2.....	50.310	25.443	24.867	24.872	-0.005
3.....	49.835	24.594	25.241	25.204	+0.037
4.....	50.053	25.251	24.802	24.797	+0.005

Av., +0.004

Here again it would seem that *N* dichromate and iodide destroy each other volume for volume in 0.02 *N* solutions so far as reasonable accuracy of analysis can determine.

Three more analyses with the same solutions were made but the stirring was done with carbon dioxide.

TABLE IV.

Titration against Hydriodic Acid of Baker's Potassium Dichromate 3 Times Recrystallized. Stirring with Carbon Dioxide.

Expt.	0.02 N KI. Cc.	0.02 N KMnO ₄ . Cc.	KI used by chromate. Cc.	Chromate present. Cc.	Deviation KI used. Cc.
1.....	50.151	25.187	24.964	24.931	+0.033
2.....	49.775	24.877	24.898	24.891	+0.007
3.....	49.895	24.810	25.085	25.106	-0.021

Av., +0.006

It is evident that this chromate also shows its theoretical oxidizing value and that the air has no influence great enough to determine with certainty.

It seemed not superfluous to test the action of air further by standardizing a comparatively crude sample of potassium dichromate with the same solutions of iodide and permanganate, using weight burets and the same precautions described already. An approximately 0.02 *N* solution was made and 10 titrations were made as described, using vigorous stirring with air in the first 5 titrations, and with carbon dioxide in the second 5. The normality of the chromate obtained with air stirring was 1.0067 and with carbon dioxide 1.0065.

The results here obtained are in accord with those of Bruhns and Kolt-hoff, and show no "super-oxidizing power" of potassium dichromate either in the presence or absence of air, that is capable of certain determination. As an illustration of the accuracy and uniformity of this method of titration it may be stated that the 15 determinations that constitute Tables I to IV are consecutive, none being rejected.

Some preliminary work has been done on the determination of iodic acid and on substances of possible interference as already mentioned.

These subjects will be continued, and it is hoped to suggest some practical applications of the method in technical chemistry. The work hitherto described was done in Grinnell College. The study of the method with its applications was resumed in Johns Hopkins University, where the great chemical library invited further study of the related literature. It was soon discovered that Crotogino,¹ in the course of his work on oxidation potentials, had long ago made in dil. sulfuric acid 3 electro-metric titrations of iodide alone, using 2, 4 and 6 cc. of 0.1 *N* iodide, and 2 others in which 2 cc. of iodide was titrated in the presence of 10 cc. of 0.1 *N* chloride and bromide, respectively. The volumes of 0.02 *N* permanganate were uniformly about 1% too large, according to its standardization with Mohr's salt. He used plug resistance boxes as a potentiometer and the stirring was by hand with the platinum electrode or a glass rod. He assigned the excess of 0.02 *N* permanganate to the formation of iodic acid seeming to confirm his previous work tending to show the formation of iodic acid when a permanganate solution was run into a hot acidified iodide solution. These results are in conflict with my own, in which, as stated in Series II and III, the iodide concentrations calculated from the permanganate were a little smaller than the results obtained with silver. Extraordinary is the fact that bromide 5 times the equivalent of the iodide did not increase the permanganate consumed whose excess was 0.1 cc. equivalent to 0.02 cc. in measuring the iodide solution.

To determine directly whether iodic acid is formed in such determinations as described in this paper, 3 titrations of 25 cc. of 0.02 *N* iodide solution were made in the usual way, stopping the addition of permanganate at the end-point, about 0.6 volt. The free iodide was completely extracted with pure benzene. The remaining solutions showed not a trace of iodine when starch solution and 5 cc. of 0.02 *N* iodide solution was added, though the same amounts of these reagents and one drop of 0.02 *N* potassium iodate solution added to the usual concentration of sulfuric acid produced a strong color which was marked when diluted to 1500 cc. Another titration was made in the same way save that permanganate was added in excess till the voltage rose to about 0.7. On extracting and testing the water-clear solution as described a color appeared which required about 0.5 cc. of 0.01 *N* thiosulfate solution to discharge. To place the question beyond doubt, another titration was made; $\frac{1}{2}$ of the solution was removed at the end-point, and 3 cc. of permanganate solution was added to the other half. On extracting and testing, the former showed no color, the latter a dense blue, which required about 7 cc. of 0.01 *N* thiosulfate. It seems certain, therefore, that iodic acid is either not formed or is destroyed by the iodide, until after the end-point has been passed. The high results obtained by Crotogino were not due

¹ Crotogino, *Z. anorg. Chem.*, **24**, 225 (1899).

to iodic acid, formed before the end-point was reached, but may well have been due to the unavoidable errors in measuring such small volumes or to his method of stirring, which would certainly cause fluctuating voltage, dropping when stirring ceased and likely to cause reading the voltages too low.

In applying the method discussed, it is practicable to use back titration if the end-point is passed, as thus shown. In the same titration the end-point was noted, several cc. of permanganate in excess was run in. Now an excess of iodide was added and the end-point again found. This was repeated 5 times, giving the ratios of volumes of iodide to permanganate 1 to 1.032, 1.031, 1.031, 1.031, 1.0305. Separate titrations using larger volumes gave 1 to 1.0306.

Summary.¹

1. Iodide in dil. sulfuric acid has been accurately titrated electrometrically with permanganate. Chloride and bromide decrease and delay the sudden rise in voltage in proportion to concentration, but chloride at least equivalent to the iodide, or 25% of an equivalent of bromide is permissible.

2. Dichromate and iodate as oxidants in 0.02 *N* and 0.05 *N* solutions may be accurately titrated by adding the solutions of either to an excess of iodide in sulfuric acid and titrating the excess with permanganate. Silver has been determined in the same way. The details for iodate and silver will be presented in a later paper.

3. The high results obtained by Crotofino in titrating iodide with permanganate were not due to the formation of iodic acid before the end-point was reached.

4. Dichromate by this method shows its theoretical oxidizing capacity.

5. A simple potentiometer permitting speed, having high resistance and accurate enough for the work is described.

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THE MOLECULAR HEAT OF HYDROGEN.

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On the general basis of the quantum theory and making use of the Bohr model of the hydrogen molecule, Krüger² has attempted to calculate

¹ The author was made aware of the work of Kolthoff (*Rec. trav. chim.*, 39, 208 (1920), through *C. A.*, 14, 320 (1920)) after this paper had been sent to press. More than a year ago he tried to titrate iodide directly with iodate and dichromate. The results at that time and obtained since reading the paper of Kolthoff have not been satisfactory, though with solutions of at least 0.05 *N* concentration and sulfuric acid as the medium, results very near the true values have been obtained with the iodate.

² Krüger, *Ann. Physik.*, 50, 346; 51, 450 (1916).