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THE COMPARATIVE VALUES OF DIFFERENT SPECIMENS OF
IODINE FOR USE IN CHEMICAL MEASUREMENTS.

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Introduction.

This paper¹ gives the results of experiments in which iodine as ordinarily prepared as a standard in volumetric analysis was compared with iodine of atomic weight purity, the medium of comparison being a sodium thio-sulfate solution.

Papers of a similar sort that were found are by Gross² and Meineke.³ Gross' paper is very brief and contains none of the original data. Meineke, on the other hand, prepared a number of specimens of iodine by different methods and through the medium of a thiosulfate solution compared them with an iodine purified by the method of Stas. His technique, however,

¹ This is the third of a series of investigations at the Ohio State Laboratory in which some fundamental point in analytical chemistry is studied by comparing the substance or operation in question with a standard substance prepared and measured with as near an approach to "atomic weight" accuracy as may be. Other similar investigations are in progress and it is hoped in time to develop new methods of preparing standard substances and new apparatus for increasing the accuracy of the important analytical measurements. The other papers are in THIS JOURNAL, 36, 2360 (1914), and 40, 1664 (1918).

² Gross, THIS JOURNAL, 25, 987 (1903).

³ Meineke, *Chem. Ztg.*, 16, 1126, 1219, and 1230 (1892).

was that of an accurate analytical procedure, rather than of a precise measurement, and therefore it seemed worth while to supplement his results by the scheme followed in this paper. Meineke's papers are rich in information about the purification of iodine and contain a wealth of experimental data.

Preparation of Materials.

Water.—"Conductivity" water was used throughout.

Starch Indicator.—A sterilized starch paste made by the method given in Treadwell's "Quantitative Analysis" was employed.

Potassium Iodide.—One of the so-called analyzed brands was used. Tests showed that no iodine was set free from its solutions under the conditions of this work.

Hydrogen Sulfide.—The gas was generated from ferrous sulfide with c. p. sulfuric acid. Before use it was washed 5 times with water.

Potassium Permanganate.—The c. p. salt was recrystallized twice in platinum. It gave no reaction for chlorine.

The Various Specimens of Iodine.—"ATOMIC WEIGHT" IODINE. One of the general methods of Baxter⁴ was faithfully followed, excepting as noted below, the cycle of purification processes being carried through three times. The exceptions were (a) a modification of the apparatus for distilling iodine from a liquid mixture and (b)

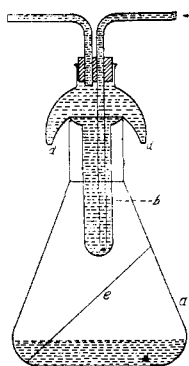


Fig. 1.

the apparatus for the final drying of the iodine at the conclusion of the wet processes of purification. The distillation apparatus is illustrated in Fig. 1. The essential feature is the condensation tube, b, about 19 mm. in diameter and long enough to project 8 or 10 cm. into the 600cc. Erlenmeyer flask, a. It is cooled by a stream of tap water, passing through it as shown in the drawing and is held in position by a bulb blown near the top. This bulb is given an umbrella shape which serves for closing the neck of the flask against loss of iodine and also for protecting it against falling dust or other contamination. By heating the mixture in the flask almost to boiling the iodine distills and solidifies on the condensation tube. There is no contamination due to bumping with consequent projection of liquid onto the iodine. A slight danger of splashing from falling drops of water that had condensed on the cold tube is eliminated by placing a narrow glass plate as shown at e. The drops strike this and glide down gently. This apparatus, which is analogous to one described in Treadwell's "Quantitative Analysis," has proved of great value in the distillation of iodine. Drying and sublimation of the iodine was effected in an apparatus made from a Hempel desiccator modified by inserting supports for carrying a number of watch glasses, and by grinding in a condensation tube which projected through the tubulure at the top. Phosphorus pentoxide was placed on the watch glasses and in the circular tray of the desiccator. Iodine to be dried is placed in a dish in the bottom of the apparatus, which is moderately warmed. The temperature of the interior at a point about midway between the top and bottom was 40°. Under these conditions iodine vapor ascends slowly over and around the phosphorus pentoxide and solidifies on the condensation tube, which is cooled with tap water. Like the distillation apparatus, this drying tower was found to have many advantages. Its use saved time because it needed no attention while in operation.

As a final note, it should be stated that all transfers of the "atomic weight" iodine

⁴ Baxter, THIS JOURNAL, 26, 1579 (1904).

from one vessel to another that occurred in the last of the series of purification operations were made in a dust-proof box equipped with rubber sleeves.

IODINE 2.—Commercial iodine was ground with potassium iodide and sublimed, and the sublimation repeated without the use of potassium iodide. The final product was then ground in a mortar and placed over calcium chloride.

IODINE 3.—This was commercial "resublimed" iodine just as received from the laboratory store-room.

IODINE 4.—Iodine recovered from titration residues and from residues from the purification of iodine by the Baxter method was the starting point of this preparation. When free iodine was present in these residues it was reduced by hydrogen sulfide and the resulting hydriodic acid neutralized by sodium hydroxide. The mixture was then evaporated in the open air, treated with manganese dioxide and sulfuric acid and the iodine distilled. This iodine was then twice dissolved in potassium iodide solution and redistilled. It was dried in a vacuum desiccator over calcium chloride for one week.

IODINE 5.—This was the same as Iodine 4, except that it was dried in the phosphorus pentoxide apparatus.

IODINE 6.—This was prepared in all respects like the "atomic weight" iodine, excepting that it was not sublimed in the phosphorus pentoxide apparatus. The product from the last distillation from potassium iodide solution was, instead, placed over sulfuric acid where it remained for 93 days before it was used.

Comparison of the Various Specimens of Iodine.

Balance and Weights.—A long-armed Troemner balance and a set of gold-plated brass weights with the fractional parts of platinum were used. These weights had been calibrated by the Bureau of Standards. All weighings were made at night in order to avoid the vibrations of the building. The method of tares was used throughout and it is believed that the weighings are defined to within 0.02 to 0.03 mg. Since there is no reason to suppose that the various specimens of iodine differed materially in density, weights were not reduced to a vacuum, but they were corrected for the different densities of brass and platinum, so that the values as finally given are those that would have been obtained had all of the weights been of platinum.

Preparation of the Iodine for Weighing.—1. In case the iodine was to be fused it was placed in a porcelain boat in the heating tube of a Richards bottling apparatus.⁵ After passing dry air over the sample for 20 to 30 minutes, the part of the tube occupied by the boat was cautiously heated until the iodine just melted. With care the iodine could be maintained in the liquid state for one or two minutes without undue loss by volatilization. The usual procedure was to keep it fused for one minute and then push the boat into a cooler part of the tube towards the bottling chamber. The bottom of the boat being then in contact with cold glass cooled while the upper part remained warm. Iodine that had sublimed on the edges of the boat volatilized again, so that in the end the only iodine visible was the hard, glassy looking cake in the bottom of the boat. During the whole operation the current of dry air was maintained and continued until everything was completely cool. The boat was then bottled and after lying in the balance case for at least an hour was weighed. The weighing bottle and empty boat had previously been put through the same process at

⁵ Richards and Willard, *THIS JOURNAL*, 32, 25 (1910).

least twice or until constant weight was reached. In the weighing of all samples a weighing bottle and boat as nearly as possible like those containing the iodine were used as a counterpoise.

The air passing through this bottling apparatus was first filtered through a 2-liter bottle filled with cotton wool. It next passed through an all-glass series of purifying and drying towers, the first one of which contained glass beads over which silver nitrate solution trickled, and the second was filled with sodium carbonate that had previously been fused and the fusion cake broken into pieces; next followed 4 towers of beads over which conc. sulfuric acid was kept flowing, and finally a tube filled with alternate layers of glass wool and phosphorus pentoxide.

2. When the sample of iodine was not to be fused, it was transferred from its container to the weighing bottle as quickly as possible and with cautions against contamination from dust.

Sodium Thiosulfate Solution.—The solution of sodium thiosulfate used throughout the work was a residuum of 5 or 6 liters from a larger lot that had been made up in December, 1918, and standardized in January, 1919, by titrating it from a volume buret against resublimed iodine prepared as described above for Iodine 2. Its value then was 0.1003 *N*. During the interval of 2 years the solution had stood in an uncolored glass bottle exposed to the light but protected by a soda-lime tube against acid fumes and carbon dioxide. When it assumed a rôle in this investigation it was placed in a dark room. The first hope that a thiosulfate solution as old as this had become constant was unfounded, for a few months' work showed a progression in the results that pointed to a gradual decrease in its iodine value. Accordingly, in the following table the final thiosulfate values of the various specimens of iodine are calculated to the value which the thiosulfate solution had on April 10, 1921.

The correction factor was calculated from the average thiosulfate solution values of 0.40000 g. of "atomic weight" iodine as found in Groups I and II, and from the corresponding values of Iodine 2, as found in Groups III, IV, and V in the table. This gives three comparable time intervals, which coincide well with the whole work, and from the data the average daily change in this thiosulfate solution in terms of weight of solution to react with 0.40000 g. of iodine was found to be 0.000787 g. This amount multiplied by the time in days between the date of an experiment and April 10, was added or subtracted, as the date demanded. The authors are, of course, aware that such a procedure is not to be recommended in precise measurements, but in their case it became a necessity in order to save the results. The error introduced does not destroy the value of the results as a contribution to analytical chemistry.

Solution and Titration of the Iodine.—Two titration flasks were employed similar in all respects excepting that one of them was closed with

a rubber stopper and the other one was entirely of glass as illustrated by Fig. 2. The ground-in stopper carried 2 tubes, a, for introducing the sodium thiosulfate solution and b, for the escape of displaced air. Loss of iodine vapor during a titration was prevented by having Tube a, dip below the surface of the liquid and by potassium iodide solution in the bends of Tube b.

The introduction of the weighed portions of iodine into this titrating flask was accomplished by first loosening but not removing the stopper of the weighing bottle and then putting the bottle into the flask. Next with the flask in an inclined position the stopper of the weighing bottle was removed with a glass hook which was quickly withdrawn and the flask closed. Two cc. of saturated potassium iodide solution was then added through Tube a, followed by a little water. By properly rotating and inclining the titrating flask the boat was brought out of the weighing bottle so that all surfaces, that is, of the weighing bottle, its stopper, which had been left in the flask, and of the boat, could be bathed in the strong potassium iodide solution. When the iodine was dissolved, the volume was made up to about 150 cc. with water and was ready for titration. This was done according to the following routine. Thiosulfate solution was added in approximately 5g. portions with intermediate mixing by shaking the flask. When all but a trace of iodine had been reduced, starch indicator was added and the titration finished.

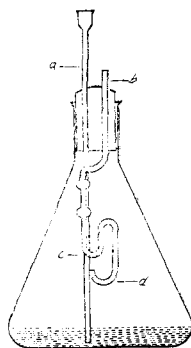


Fig. 2.

In order to reach a uniform end-point 4 comparison flasks of the same size and color of glass as the titrating flask were prepared and charged with solutions in every way like that in the titration flask at the end of a titration excepting in respect to the content of iodine. Comparison flask No. 1, contained no iodine and Nos. 2, 3 and 4 had amounts of iodine equivalent respectively, to 0.006 g., 0.012 g., and 0.018 g. of the thiosulfate solution. These varying amounts of iodine gave with starch a set of color standards by which it was easy to follow the approach of the end-point in the solution being titrated. In any event each end-point was tested by titrating back with an iodine solution.

It was found that a more uniform end-point could be obtained with the light from an ordinary tungsten bulb than with the varying light of the sun. The bulb was supported a few centimeters above the desk top with a sheet of white paper above it to reflect the light downwards upon other white paper on the desk. Upon this white surface on the desk were placed the color standard flasks and from time to time the titrating flask for comparison. The observations were made from a point above the light bulb. In this way the end-points were reproducible within 0.006 g. of the thio-

sulfate solution. Another reason for preferring artificial light to that of the sun is the action of the latter in liberating iodine. Concentrated solutions of potassium iodide became distinctly yellow in 10 minutes in direct sunlight.

TABLE I

Iodine	ANALYTICAL RESULTS					
	Iodine	Thio-sulfate solution	Thio-sulfate solution calculated to 0.40000 iodine	Average	Average corrected for change in thio-sulfate solution	Purity of iodine
G.	G.	G.	G.	G.	G.	%
Group I, April 10, 1921, "Atomic Weight" Iodine, not fused.	0.39206	32.3748	33.030			
	0.45868	37.8628	33.019			
	0.48325	39.8879	33.014	33.030	33.030	100.000
	0.49642	41.0163	33.050			
	0.57185	47.2322	33.038			
Group II, April 29, 1921, "Atomic Weight" Iodine, fused.	0.54560	45.0777	33.049			
	0.33932	28.0087	33.018			
	0.40043	33.0710	33.035	33.045	33.030	100.000
	0.57602	47.6233	33.071			
	0.49461	40.8684	33.051			
Group III, Jan. 18, 1921, Iodine 2, resublimed once from KI and once alone; ground and kept over CaCl ₂ .	0.37134	30.6151	32.978			
	0.46267	38.1505	32.983			
	0.55278	45.6171	33.009			
	0.46183	38.0386	32.946	32.973	33.038	100.024
	0.42732	35.1963	32.946			
	0.41060	33.8484	32.975			
Group IV, Feb. 16, 1921, Iodine 2, as described above.	0.44523	36.7008	32.972			
	0.54446	44.9246	33.005			
	0.52526	43.3212	32.991	32.997	33.039	100.018
	0.46477	38.3382	32.995			
Group V, April 20, 1921, Iodine 2, as described above.	0.46002	37.9478	32.995			
	0.49583	40.9530	33.038			
	0.49537	40.9209	33.043	33.044	33.036	100.018
	0.51626	42.6567	33.051			
Group VI, Feb. 17, 1921, Iodine 3, product just as received from store-room, except that it was fused before weighing.	0.46010	38.0061	33.042			
	0.26374	21.7366	32.968			
	0.36245	29.9089	33.008	32.995	33.036	100.018
Group VII, Feb. 23, 1921, Iodine 3, as above, but not fused before weighing.	0.34615	28.5655	33.009			
	0.35231	29.0509	32.984			
	0.40486	33.4021	33.002			
	0.38186	31.4888	32.984	32.994	33.030	100.000
	0.43344	35.7709	33.011			
	0.41145	33.9214	32.977			
	0.46869	38.6702	33.003			

Group VIII, April 21, 1921.	0.45876	37.8893	33.036			
Iodine 3, as above, but not fused.	0.56198	46.4199	33.041	33.041	33.032	100.006
	0.49452	40.8364	33.031			
	0.50921	42.0799	33.055			
Group IX, March 17, 1921,	0.45363	37.3096	32.899			
Iodine 4, recovered from residues; dried over CaCl ₂ for one week but not sublimed.	0.28391	23.3198	32.854	32.877	32.889	99.57
Group X, March 22, 1921,	0.36848	30.4221	33.024			
Iodine 5, same as No. 4, excepting that it was sublimed in P ₂ O ₅ apparatus.	0.39392	32.5201	33.022	33.023	33.038	100.024
	0.46061	38.0158	33.014			
	0.38952	32.1678	33.033			
Group XI, Feb. 14, 1921,	0.53442	43.9857	32.921			
Iodine 6, "Atomic Weight" Iodine; not sublimed but kept 93 days over H ₂ SO ₄ .	0.40481	33.3249	32.929	32.928	32.971	99.82
	0.42985	35.3811	32.924			
	0.42995	35.4024	32.936			
Group XII, May 5, 1921,	0.42324	34.9834	33.062			
"Atomic Weight" Iodine after 7 hours exposure in current of air saturated with water vapor.	0.50817	41.9983	33.058			
	0.54587	45.1022	33.050	33.053	33.033	100.009
	0.49967	41.2612	33.031			
	0.43242	35.7428	33.063			

Discussion of Results.

With the exception of Nos. 4 and 6, the specimens of iodine examined agreed within 0.02% with the "atomic weight" iodine. The deviation from the "atomic weight" iodine, except as noted, was always above 100%, which would seem to indicate such impurities as chlorine and bromine. This, however, is unlikely, since the unpurified iodine, No. 3, has a smaller positive error than the others. It would also seem from the nature of its preparation that Iodine 5 would hardly be contaminated that way. The cause is seemingly in a systematic error that has escaped detection.

Evidence of water in No. 4 is found in the fact that it rose in value when put through the phosphorus pentoxide drying tower.

The low value of No. 6 could be accounted for on the basis of a statement by Treadwell,⁶ that iodine takes up sulfuric acid when dried over it. This statement, however, can hardly be accepted in the light of evidence to the contrary in the literature. Baxter⁷ dried some of his atomic weight iodine over sulfuric acid and makes no mention of it as a possible impurity that was removed in the subsequent sublimation of the iodine. Meineke⁸ reports several experiments in which iodine was exposed for days over

⁶ Treadwell, "Quantitative Analysis," John Wiley and Sons Co., 3rd Ed., p. 646.

⁷ Baxter, *THIS JOURNAL*, 32, 1594 (1910).

⁸ Meineke, Ref. 3, pp. 1126, 792.

sulfuric acid without evidence that any of the acid was taken up by the iodine.

It is the belief of the authors that Iodine 6 still contained water in spite of its long exposure over sulfuric acid. An inspection of Nos. 4 and 6 shows that they had one point in common, namely, distillation from water and condensation on a cold surface on which water was condensing at the same time in contact with the iodine. This condensation in the wet way was the last purification process, except the drying (?) over a desiccating agent to which Nos. 4 and 6 were subjected. No. 4, undoubtedly contained water (see above). Lack of time and material made it impossible to test No. 6 directly, and until the point can be investigated experimentally, the hypothesis is offered that iodine when it solidifies in the presence of liquid water entrains some of the water in a way that withstands months of exposure over a desiccating agent. The complete removal of water from iodine demands dry sublimation in the presence of a desiccating agent.

Is Iodine Hygroscopic?—Meineke⁹ exposed dry iodine for 5 days to the air of his laboratory and reports that the change observed could be ascribed to experimental errors. Powdered iodine exposed under a bell jar with a dish containing water took up 0.09% of water in 48 hours. Iodine crystals when subjected to the same conditions took up only 0.05% of water in 5 days. An exposure of 10 days over sulfuric acid brought these last two specimens back to 100.00%. Meineke's iodines had all been sublimed in the dry way and therefore the situation is not comparable with that of No. 6, above.

In this investigation, the following experiment was made to test the hygroscopic nature of iodine. About 5 g. of the "atomic weight" iodine was spread in a thin layer in a glass tube and a current of air previously bubbled through water was passed over it for 7 hours at the rate of about 9 liters an hour. The results are given in Group XII, of the table, and show that if any water was taken up, the amount was well within the experimental errors. This experiment and those by Meineke show that iodine is not hygroscopic to a degree that would affect analytical work.

A Possible Contribution to the Data of Adsorption.—One of Meineke's experiments shows that when iodine is finely divided and exposed to air saturated with water vapor, a small amount of water is taken up. It is reasonable to suppose that this water is adsorbed on the surface of the solid iodine, and the question then arises as to what effect the relatively high vapor pressure of the iodine has on such adsorption. If adsorption is a surface phenomenon, then a surface like that of an iodine crystal which is constantly sending off molecules and therefore constantly presenting a fresh surface must introduce complications. The rate of adsorption under

⁹ Ref. 3, p. 1126.

such conditions would be slow and if later such a solid were placed in an atmosphere free from water vapor the portion adsorbed would soon be given up because the surface holding it would have disappeared. One would therefore expect solids with high vapor pressures to be slightly or not at all hygroscopic.

The Use of a Rubber Stopper in the Titrating Flask.—The titrations of Group VII were made in a flask closed with a rubber stopper, and those of the strictly comparable Table VIII were carried out in the all-glass apparatus. The manipulation was the same in both cases. The agreement between these two sets of results is almost perfect, and therefore the use of a rubber stopper may be permitted in analytical operations.

Summary.

Some new forms of apparatus for the preparation and handling of pure iodine are described.

Various specimens of purified iodine were compared with a highly purified iodine. The agreement was found to be close; 0.024% was the maximum deviation.

Experiments are described which show that a rubber stopper may be used for closing the flask in which iodine is titrated.

The usual method, as given in text-books of analytical chemistry, of drying iodine by exposing it in a desiccator with a drying agent, is questioned if the iodine had previously solidified in the presence of liquid water.

The hygroscopic properties of iodine are discussed.

A suggestion is made that solids like iodine that have a measurable vapor pressure at room temperature possess peculiar adsorptive properties due to the fact that a fresh surface is being continually exposed.

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