Summary.

It is shown in this paper that in the decomposition of the alkali amalgams by means of hydrochloric acid, a point is reached at which there is a sudden increase in the surface tension of the amalgams, and that this increase in surface tension is accompanied by the sudden evolution of a cloud of minute hydrogen bubbles, and by a sudden decrease in the solution pressure of the amalgams.

CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS,
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COLORIMETRIC DETERMINATION OF DISSOLVED OXYGEN IN WATER.

G. B. FRANKFORTER, G. W. WALKER AND A. D. WILHOIT.

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Dissolved oxygen is becoming an important factor in the regular sanitary analysis of water. The amount of free oxygen will frequently enable the analyst to diagnose the sample with accuracy. If a sample of water contains less than the normal amount of dissolved oxygen, one may conclude that the water has, during its recent history, contained a considerable quantity of organic matter or some other reducing reagent like iron or perhaps that it has come from some deep underground current where it has been excluded from the air for a long time as in the case of very deep wells.

While the variation in the amount of dissolved oxygen is not so great as the variation in the amount of some of the other sanitary constituents in water, it is nearly always sufficient to enable one to draw a pretty definite conclusion as to the source and history of the sample. From a large number of analyses of water from a great many different sources, we have found that the volume of oxygen usually lies between 1 and 7.5 cc. per liter. In extreme cases, we have found samples to vary from a trace to 10 cc. per liter. In many of the artesian wells we have found the oxygen to run as low as 0.3 cc. per liter. Samples from the iron mines of Northern Minnesota frequently contain only a mere trace, while samples from some of the peat bog springs do not contain even a trace. On the contrary, the water from the Mississippi river as it flows over the St. Anthony Falls in winter, contains as high as 10.6 cc. per liter, while the same water, collected just below the inlet of a large sewer, contained only 3.2 cc. per liter. Samples from the iron springs of the northern part of this state and from peat bogs, rarely ever contain more than a trace of oxygen.

In the beginning of this work, various methods of determining oxygen were used. The boiling out method was first tried and the Reichardt and Tenax apparatuses were tested. The results, on the whole, were satisfactory but the methods required so much time that they were soon abandoned and the methods of Winkler and Thresh substituted. These methods likewise gave satisfactory results if carried out with extreme care, but these also seemed too long to become universal methods in the everyday sanitary analysis of water.

While in search for a method which would be rapid and in keeping with the general methods of water analysis, we were naturally led toward colorimetric methods. After numerous experiments, a method depending upon the change in color of cuprous ammonium chloride when brought in contact with oxygen, was selected as being the most promising. On looking up the literature, however, it was found that Ramsay and Homfray[1] had used the chloride with satisfactory results. The apparatus used by them was a modification of the Mills colorimeter, arranged so as to protect the sample from aeration by a film of oil in transferring from collecting bottle to colorimeter and also during the operation. From the excellent results obtained by the above-mentioned authors, we immediately selected this method as exactly in line with the general colorimetric methods used in the sanitary analysis of water. In carrying out the process, however, various difficulties were encountered. The first difficulty experienced was in the preparation of a perfectly colorless cuprous ammonium chloride solution. We were able to prepare apparently pure cuprous chloride but we were not able to prepare the double salt solution without a trace of color. So much depended upon the preparation of a perfectly colorless solution that it seemed advisable to try, at least, to construct an apparatus in which a solution of the pure, colorless cuprous double salt could be prepared and kept ready at all times for use.

The first apparatus tried was made by using small aspirator bottles as receptacles for the hydrochloric acid and the ammonia necessary in the preparation of the cuprous ammonium reagent. A small separatory funnel and a small calcium chloride jar were used as reservoirs for the cuprous chloride and the ammonium double salt solutions. These different parts were connected by means of rubber corks and rubber connectors. The apparatus was soon discarded on account of the fact that the blue color of cupric ammonium chloride would appear around the corks and rubber connectors in a few minutes after the preparation of the cuprous double salt. So rapidly did the blue color appear that it was practically impossible to prepare a colorless solution, much less to keep it colorless for any length of time. Every effort to make the rubber impervious to oxygen was unsuccessful. Best results were obtained by coating the rubber connectors with a heavy coating of shellac, afterwards covering the shellac with gutta percha. Even with these precautions, a distinct blue color would appear around the rubber connections in an hour or two.

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[1] *J. Soc. Chem. Ind.*, 20, 1071 (1901).

The fact that shellac and gutta percha did not prevent the blue color from forming led us to suspect that the blue color may have come from the rubber. It was found, however, that if the rubber connectors were protected from the air by an atmosphere of hydrogen, the blue color would not appear.

With the rubber connectors coated as indicated above we were able to prepare a solution which gave satisfactory results, if used immediately after its preparation. A large number of determinations were made with this apparatus but the fact that the reagent could not be kept in a colorless state for any length of time, led to the adoption of the apparatus illustrated in Fig. 1. This apparatus is made entirely of glass, thus removing most of the difficulties encountered in the first form. By eliminating the use of rubber corks and connectors we were able to keep the colorless cuprous solution for a long time and by substituting burettes or graduated tubes for aspirator bottles, measured quantities of acid and ammonia could be used, thus keeping the double salt solution at constant strength. The following is a description of the apparatus: *A* is a burette

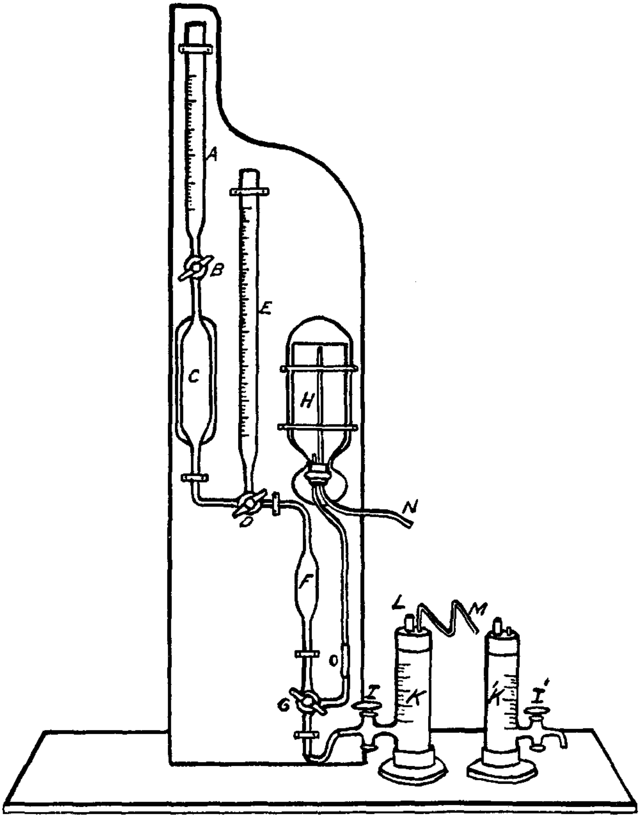

Fig. 1.

connected, by means of a stop-cock *B*, with *C*, a reservoir for preparing and keeping cuprous chloride. *E*, a second burette for supplying ammonia, is connected with *C* and *F* by means of a three-way cock, *D*. *F* is a mixing bulb for the preparation of pure cuprous ammonium chloride. *G* is a three-way cock connecting *F*, by means of a capillary tube, with the colorimeter *K*, and *H* is a reservoir for holding the sample of water. Reservoir *H* contains a tube, *N*, which extends nearly to the top of the reservoir, the lower end of which is connected with a Kipp hydrogen generator for replacing the water, as it is drawn out, with hydrogen. *K* is arranged with a stop-cock, *I*, and a cork through which passes a large tube *L*, the lower end of which is closed by a disc firmly cemented to the tube. Comparisons with the standard are made by looking down through this tube. *M* is an outlet for air and water in completely filling the colorimeter. *K'* is a similar colorimeter tube for making comparisons. To charge the apparatus, copper wire is first introduced into *C* through *A* and *B*, the opening in the stop-cock *B* being large enough to admit pieces of copper wire. *C* is then filled with a saturated solution of cuprous chloride in hydrochloric acid and the whole allowed to stand until any cupric chloride, which may have been formed in filling the reservoir, has been reduced. *A* is then filled with concentrated hydrochloric acid to be added as the cuprous chloride is drawn out through *D* into *F*, where it is converted into the double salt. *F* is filled with oxygen-free water from *H* by opening the three-way cocks *G* and *D*. When the water reaches *D*, *G* and *D* are closed, *E* is filled with ammonia and the apparatus is ready for making the double salt. *C* is now connected with *F*, and *B* is cautiously opened, when cuprous chloride will pass into *F* as soon as *G* and *I* are opened. By noting the height of the acid in *A*, the quantity of saturated cuprous chloride introduced into *F* may be accurately measured off. In charging the apparatus, 2 cc. of the chloride are run in and 8 cc. of ammonia, the capacity of *F* being about 10 cc. This amount of ammonia is sufficient to convert all the chloride into the double salt. In the accompanying tables, 2 cc. of the reagent were used in each determination. It was made by mixing 0.5 cc. of the cuprous chloride and 1.5 cc. of the strong ammonia.

The manipulation is as follows: *H* is completely filled with the sample of water, corked, placed in position on the stand and connected with the apparatus at *O*. *N* is connected with a hydrogen generator. By opening *I*, connecting *H* with *K* by means of the three-way cock *G*, the colorimeter tube *K* is completely filled with the sample. Care must be taken that the small bubbles of air which cling to the cork are removed. The colorimeter tubes *K* and *K'* are so constructed that when the corks are placed in position, they each hold exactly 102 cc. After the colorimeter had been carefully filled with the sample, 2 cc. of the cuprous ammonium chloride from *F* are introduced. This is accomplished by connecting *F* with *K*, opening B and cautiously opening D. When 0.5 cc. of the reagent has been introduced into *K*, *B* is closed and *D* is turned so as to connect *E*, containing ammonia, with K. 1.5 cc. of the reagent are introduced into *K*, making a total of 2 cc. If this is done with sufficient speed, none of the reagent passes out of the tube *M*, and there is left in the colorimeter just 100 cc. of the sample of water and the 2 cc. of reagent. *G* and *I* are now closed and the colorimeter which is connected with the apparatus by a flat ground joint and rubber tube, may be removed for comparison. As soon as the cuprous solution comes in contact with the oxygen in the water, the blue color appears, the intensity of which is measured by the amount of free oxygen present in the water.

The comparison is made by means of *K′*, a second colorimeter tube, and a standard solution of cupric chloride of such strength that 1 cc. of the solution will be equivalent to 1 cc. of oxygen in a liter of water when the quantity of water taken for analysis is 100 cc.

Such a standard copper solution is prepared by dissolving 1.1364 grams of pure copper in aqua regia, evaporating off the excess of acid, dissolving in water and making up to one liter. One cc. of this solution is equivalent to 0.1 cc. of oxygen as indicated by the following equation:

$$Cu_2Cl_2 + 2HCl + O = 2CuCl_2 + H_2O.$$

The ratio between the weight of copper and oxygen in this equation is 127.2 : 16. Substituting the weight of 0.1 cc. oxygen under standard conditions we have the equation

$$127.2 : 16 :: x : 0.00014295.$$

$$X = \frac{127.2 \times 0.00014295}{16} = 0.00113645,$$ the equivalent of copper in 0.1 cc. or 1.13645 grams in a liter.

In the regular analysis, the sample of water is treated as indicated above and the color produced by the cuprous reagent is matched by a known quantity of standard cupric solution. This is accomplished by placing a known amount of the standard solution in the second colorimeter tube with sufficient ammonia to convert the copper into the double salt, and making up to 100 cc. with water. An excess of the standard is taken so that the color is deeper than that of the sample. The standard solution is now drawn off from the stop-cock *I′* until the shades of color in the two tubes are the same. From the quantity of standard solution necessary to match the color in *K*, the amount of oxygen may be easily determined. When 100 cc. of water are taken, the number of cubic centimeters of standard will represent directly the number of cubic centimeters of oxygen in a liter of water.

It was found necessary, in making more than a single determination, to fill the space in *H* occupied by the sample drawn off for analysis by some gas which does not contain oxygen. Several gases were tried. Nitrogen gave good results but it was too difficult to obtain in pure form to be satisfactory. Carbon dioxide did not seem to give satisfactory results. Hydrogen was used in nearly all of the following analyses, although the oxygen seemed to diminish if the water remained any length of time in contact with hydrogen.

In making the first readings it was found difficult to obtain concordant results as the shades of color produced by small amounts of the reagent were not distinct. This was especially true when the color was deep. The limit of accuracy was therefore determined by adding small quantities of the standard to a solution which already contained a known quantity of the standard solution. It was found that the eye, without the aid of a colorimeter, could not note the change produced by 0.2 cc. of standard solution in 100 cc. of water unless the quantity of standard solution used was small. The sensibility decreased with the increase in the amount of standard solution, so that after 5 cc. of the standard had been added, no distinct change in color appeared on adding 0.2 cc. of the standard.

The tables which follow were obtained by using a known quantity of the standard in one colorimeter tube, and the same quantity plus the increase indicated in the tables in the other. The colors were then matched by allowing the solution in the denser tube to run out until the colors were the same. From the amount of solution left in this tube, the limit of accuracy was determined.

The following table was made in ordinary diffused light without the aid of the colorimeter:

STANDARD COPPER SOLUTION.

Number of cc. taken plus the following:	0.2	0.4	0.6	0.8	1.0	2.0 cc.
1	1.12	1.31	1.56	1.81	1.89	2.9
2	2.14	2.42	2.50	2.65	2.91	3.85
3	3.10	3.34	3.46	3.69	3.94	3.92
4	4.2	4.30	4.45	4.86	4.95	6.00
5	5.1	5.30	5.56	5.65	5.85	6.68
6	6.0	6.21	6.44	6.68	6.80	7.92
7	7.0	7.10	7.5	7.75	7.89	8.68
8	8.0	8.0	8.5	8.55	8.6	9.80
9	9.0	9.0	9.6	9.9	9.9	10.6
10	10.0	10.0	10.0	10.4	11.1	12.1

The above results do not indicate very great accuracy. Somewhat better results were obtained by using a Krüss colorimeter, making comparisons in bright diffused light. Under these conditions the following results were obtained:

STANDARD COPPER SOLUTION.

No. cc plus	0.2	0.4	0.6	0.8	1.0 cc.	2.0 cc.
1 gave	1.15	1.29	1.46	1.68	1.92	2.94
2 "	2.12	2.50	2.71	2.72	3.11	3.9
3 "	3.11	3.28	3.5	3.68	3.84	5.0
4 "	4.20	4.31	4.45	4.7	5.10	6.14
5 "	5.08	5.50	5.70	5.90	6.11	4.97
6 "	6.05	6.40	6.54	6.90	6.98	7.92
7 "	7.00	7.20	7.50	7.84	7.84	8.85
8 "	8.0	8.20	8.50	8.60	8.96	10.20
9 "	9.0	9.1	9.3	9.60	9.80	10.90
10 "	10.0	10.2	10.5	10.70	10.7	11.85

The apparatus was further tested, after the above tables had been made by determining the amounts of oxygen in pure water after saturating with air at different temperatures. The following numbers, each of which represents an average of three analyses, are compared with results obtained by Roscoe and Lunt:[1]

	Colorimetric.	Roscoe and Lunt.
1 liter of water saturated with air at 15° gave.....	6.81	6.96
1 liter of water saturated with air at 20° gave.....	6.22	6.28
1 liter of water saturated with air at 24° gave.....	5.80	5.84
1 liter of water saturated with air at 26° gave.....	5.52	5.68
1 liter of water saturated with air at 30° gave.....	5.47	5.43

Determinations of dissolved oxygen in natural waters were now begun. A large number of determinations were made. The following is a table of some of the analyses as compared with results obtained by other methods:

		Colorimetric. cc.	Winkler. cc.	Reichert cc.	Thresh. cc.
Distilled water	1	5.80	6.59	5.40	5.60
Shaken with air	2	5.80	5.42	5.80	5.65
At 24°	3	5.64	5.63	5.45	5.60
Average............		5.74	5.88	5.55	5.61
Hydrant water	1	3.96	4.65	3.95	4.12
At 20°	2	4.22	4.12	4.05	4.00
	3	4.22	4.20	4.20	4.05
	4	4.25	4.20	3.90	4.10
Average............		4.16	4.13	4.02	4.07
Spring water	1	6.43	6.21	6.10	6.32
At 14°	2	6.30	6.20	6.40	6.28
	3	6.30	6.10	6.46	6.24
Average............		6.34	6.17	6.32	6.28

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[1] *J. Chem. Soc.*, **55**, 552.

		Colorimetric. cc.	Walker. cc.	Reichert. cc.	Thresh. cc.
Bog Iron Spring	1	0.30	0.25	0.21	0.32
	2	0.30	0.42	0.41	0.30
	3	0.26	0.46	0.51	0.29
Average		0.29	0.37	0.37	0.30
Mississippi River	1	6.50	6.22	6.41	6.42
	2	6.70	6.40	6.51	6.40
	3	6.40	6.18	6.32	6.45
Average		6.53	6.27	6.41	6.42
Artesian water	1	0.44			0.42
	2	0.48			0.40
	3	0.42			0.40
Average		0.44			0.41

In making the above determinations, we were surprised at the rapidity with which oxygen is absorbed by oxygen-free water or by samples very low in oxygen. In the case of certain artesian and bog iron waters, the samples had to be very carefully protected from the air in order to obtain accurate results.

That we might get some idea of the rapidity with which oxygen is absorbed by water, experiments were made on oxygen-free water by introducing a known quantity of air for a given time and determining the amount of oxygen which had been absorbed. A two-liter flask was filled with oxygen-free water. A known quantity of the water was drawn off and the space in the flask filled with air. At given intervals after the air had been introduced, oxygen determinations were made.

Results obtained were as follows:

2000 cc. water: 100 cc. gave 0.00 cc. O.
1900 cc. water: 100 cc. air: after 30 min. 100 cc. gave 0.27 cc. O.
1800 cc. water: 100 cc. air: 100 cc. H: after 1 hr. 100 cc. gave 0.32 cc. O.
1700 cc. water: 100 cc. air: 200 cc. H: after 2 hrs. 100 cc. gave 0.42 cc. O.
1600 cc. water: 100 cc. air: 300 cc. H: after 3 hrs. 100 cc. gave 0.51 cc. O.
1500 cc. water: 400 cc. air: 400 cc. H: after 5 hrs. 100 cc. gave 0.58 cc. O.

From the above table, it would appear that at the end of 5 hours, 9 cc. of the 20 cc. of oxygen introduced had been absorbed by the water. It will be noticed that the ratio of absorption decreased rapidly. At the rate of absorption of oxygen during the first half hour, the 20 cc. introduced would have all been absorbed in about 5 hours. The decrease in absorption was doubtless due to the dilution with hydrogen and to a partial saturation of the water with air.

Contrary to expectations, we had no serious difficulty with the apparatus. On several occasions we have had some little trouble with the three-way stop-cocks, especially after the apparatus had stood unused for some time. That this trouble was not serious, is born out by the fact that more than one thousand determinations have been made with the first glass apparatus constructed, and it is in perfect condition at the present time. It does require some little skill to manipulate the apparatus. However, with a little experience, accurate determinations of oxygen may be easily and rapidly made.

UNIVERSITY OF MINNESOTA, MINNEAPOLIS.

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.]

A VOLUMETRIC METHOD FOR THE DETERMINATION OF BARIUM.

BY ARTHUR E. HILL AND WILLIAM A. H. ZINK.

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Introduction.—Volumetric methods for the determination of barium appear to be few in number and somewhat limited in application. Sutton enumerates five methods in all, of which the best known is probably the direct titration of the barium compound in alkaline solution with standardized potassium dichromate[1] until the supernatant liquid assumes a yellow color. The precipitate may also be filtered and washed, reduced by a measured excess of a ferrous salt, and the residual ferrous iron titrated with potassium permanganate.[2] Barium hydroxide or carbonate may be titrated directly with standardized acid,[3] while the neutral salts may either be titrated with sodium carbonate, using phenolphthalein as indicator,[3] or may be precipitated with ammonium hydroxide and carbonate and the washed barium carbonate titrated with standardized acid.[4] The new method here proposed depends upon the precipitation of barium as iodate and upon the oxidizing action of this compound upon an iodide solution, with subsequent titration of the free iodine with sodium thiosulphate.

Discussion of the Method.—The solubility of barium iodate in pure water is given[5] as 0.028 g. of salt, or about eight mg. of barium, per hundred cc. of solution at 25°, an amount too large to admit treatment of the compound as an insoluble salt. In accordance with the theory of electrolytic dissociation, however, it might be expected that the solubility could be reduced to a negligible amount by the presence of a sufficient excess of a soluble iodate, provided that the barium iodate approximates

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[1] Sutton, *Volumetric Analysis, London,* 1904, p. 161.

[2] *Ibid.*, p. 162. See also Mohr, *Titrirmethode,* Braunschweig, 1886, p. 346.

[3] *Ibid.*, p. 69.

[4] *Ibid.*, p. 70.

[5] Trantz and Anschütz, *Z. physik. Chem.*, **56**, 238 (1906).