A COMPARISON OF METHODS FOR DETERMINING DISSOLVED OXYGEN IN WATER AND SEWAGE

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Dissolved oxygen determinations are of great value in the control of sewage disposal plants and as an index of the purity of the water in streams. Accuracy is necessary, but ease of manipulation is also of importance. Although numerous methods have been proposed, few have survived the tests of practicability and accuracy. In the last report of the Committee of the American Public Health Association on Standard Methods of Water Analysis, the Winkler method has been chosen as the standard. The Levy method is an optional method of the committee on standard methods of the American Public

Health Association, and has been used to a certain extent, but has the disadvantages of requiring special apparatus and a blank determination in each case. These two methods are practically the only ones in use in this country. A brief description of the chemistry of each method follows.

In the Levy method the sample is collected in a special pipette, into which is introduced an accurately measured quantity of ferrous ammonium sulfate ($FeSO_4(NH_4)_2SO_4$); a solution of sodium hydroxide ($NaOH$) is then added; ferrous hydroxide ($Fe(OH)_2$) is formed and part of this is then oxidized to ferric hydroxide ($Fe(OH)_3$) by the dissolved oxygen present. Sulfuric acid (H_2SO_4) is then added and the remaining ferrous sulfate ($FeSO_4$) is titrated with standard potassium permanganate ($KMnO_4$). An equivalent volume of water is treated with the same volume of reagents, but the sulfuric acid (H_2SO_4) is added first to prevent oxidation. The difference between the titration of the blank and sample will give the amount of ferrous salt oxidized by the dissolved oxygen in the water; the dissolved oxygen content in parts per million may be calculated from this.

In the Winkler method the sample is collected in a glass-stoppered bottle, and solutions of manganous sulfate $MnSO_4$, and a mixture of sodium hydroxide, $NaOH$, and potassium iodide, KI, added. The manganous sulfate and sodium hydroxide form manganous hydroxide, $Mn(OH)_2$; part of this is oxidized to manganese oxy-hydroxide, $MnO(OH)_2$ by the dissolved oxygen present in the water. Then sulfuric acid is added; this dissolves the precipitate and liberates free iodine from the potassium iodide according to the following equation:

$$MnO(OH)_2+2H_2SO_4+2KI=MnSO_4+K_2SO_4+3H_3O+I_2$$

The amount of iodine liberated is proportioned to the amount of dissolved oxygen present; the free iodine is titrated with standard sodium thiosulfate, ($Na_2S_2O_3$), using starch paste as an indicator. Dissolved oxygen is reported in parts per million.

The Levy and Winkler methods have both been checked with the gasometric method on aerated distilled water. The Levy method has sometimes been condemned because it has seemed to give variable results[1]. On the other hand, it has been recommended because it is claimed that nitrites do not affect its accuracy.

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[1] Chlopin; Arch. f. Hygiene, 32, 294-309, 1898. Tiemann and Preusse; Ber., 12, pp. 1784-5.

The Winkler method checks with the gasometric method with uniformly good results[1]. This method gives high results if nitrites are present in the solution. Organic matter is said to reduce the iodine to some extent. "Standard Methods" reads, "If nitrites be present, correction must be made." This correction is not proportional to the amount of nitrite present since the reaction is catalytic. The first reaction is,

$$HNO_2+HI=H_2O+NO+I.$$

The nitric oxide then combines with oxygen from the air to form nitrous acid again, and this liberates more iodine. Winkler appreciated the fact that the second reaction does not take place until the iodine solution is exposed to the air, and oxidized the nitrous acid quantitatively in the bottle, by forming manganic chloride ($MnCl_3$) before the addition of potassium iodide. In a separate sample the amount of manganic chloride required for the destruction of the nitrous acid (HNO_2) was determined. The equivalent of this amount, in terms of dissolved oxygen, is deducted from the total dissolved oxygen.

Two modifications have been proposed for counteracting the effect of nitrites. The first was proposed by Rideal and Stewart[2]. This modification is based upon the principle that nitrites and organic matter may be oxidized by potassium permanganate in acid solution. A few drops of sulfuric acid are first added, then an excess of permanganate. After allowing the oxidation to proceed for 20 minutes, a strong solution of potassium oxalate ($K_2C_2O_4$) is added; this is followed by the usual Winkler procedure.

The second modification was proposed by Hale-Melia[3] This modification is evidently based upon the principle of the suppression of both nitrite reactions by the suppression of the hydrogen ion concentration. In this modification, after the sample has been acidified in carrying on the usual Winkler procedure, an excess of potassium acetate, $KC_2H_3O_2$, is added. This reacts with the sulfuric acid, as follows:

$$H_2SO_4+2KC_2H_3O_2=2HC_2H_3O_2+K_2SO_4$$

Acetic acid has a low hydrogen ion (H^+) concentration; Hale and Melia claim that the interaction of HNO_2 and KI does not take place under these conditions.

In considering Hale and Melia's modification, Elvove[4] has shown that iodine is destroyed by potassium acetate when

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1. Winkler; Ber. 21, 2843-54, 1888. Kisch; Zeit. Angen. Chem., 1891, 105-8. Chlopin; Arch. f. Hyg., 27, 18-33, 1896. Spitta; Arch. f. Hyg., 38, 220, 1900. Birge and Juday; Wis. Sur. Bull., 22, 11-12.
2. Analyst, 26, 141-8.
3. Jour. Ind. and Eng. Chem., Dec. 1913, pp. 978.
4. Bull. 96, U.S. Hyg. Lab. pp. 26.

the sample stands for a long time before titration. If the potassium acetate is added from 15 to 30 minutes before the titration is carried out, the amount reduced is negligible.

As to organic matter, Hale and Melia claim that the iodine is not reduced to an appreciable extent by the organic matter present in mixtures of sewage and water.

The importance of comparing these methods has been realized by the Committee of the Laboratory Section of the American Public Health Association and a subcommittee was appointed in 1914 to undertake a comparative study to determine the accuracy, ease of manipulation and adaptability for laboratory and field work of the four methods. The chairman of the subcommittee, Professor E. B. Phelps, outlined the work for the committee.

In this paper the results and conclusions from my experimental work on these four methods are presented.

EXPERIMENTAL

Distilled water was aerated, and after 24 hours, its dissolved oxygen content was determined by both the Levy and Winkler methods.

Then .2 parts per million as nitrite was added in the form of sodium nitrite ($NaNO_2$) and the Levy Winkler, Hale Melia and Rideal-Stewart determinations made. Three samples were taken for each determination. Enough sodium nitrite was then added to bring the N as nitrite content up to .5 parts per million and the dissolved oxygen was again determined by the four methods. The averages of three determinations are reported in Table I. All except the Levy have been corrected for the volume of reagents introduced, as Winkler[1] claims that the concentrated solutions do not contain any dissolved oxygen. The standard permanganate for use with the Levy method and the standard thiosulfate for the other methods were checked against each other a number of times, and both solutions were found to be correct.

TABLE I.

	Aerated, distilled, H_2O	.2 p.p.m N as nitrite	.5 p.p.m. N as nitrite
Levy	8.23	8.17	8.17
Winkler	7.64	8.00	8.24
Rideal-Stewart		7.90	7.70
Hale-Melia		7.95	7.71

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[1] Zeit. Anal. Chem., 11, pp. 665.

The Levy values do not increase with nitrite but remain about the same as with distilled water—uniformly higher than the Winkler. The Winkler is .36 p.p.m. high with .2 p.p.m. N as nitrite, .60 p.p.m. high with .5 p.p.m. in N as nitrite Rideal-Stewart and Hale-Melia values are practically the same and check fairly well with the standard Winkler value on the same water, nitrite-free

The same procedure was followed with a second batch of samples with the exception that .5 and 1.0 p.p.m. N as nitrite were added. The results are shown in Table II.

TABLE II.

	Aerated, distilled, H_2O	.5 p.p.m. N as nitrite	1.0 p.p.m. N as nitrite
Levy	8.35	7.95	7.95
Winkler	7.58	7.97	8.79
Rideal-Stewart		7.48	7.56
Hale-Melia		7.84	7.61

Levy values are uniformly higher than the Winkler standard on distilled water. The Winkler is .39 p.p.m. high with .5 p.p.m. N as nitrite, 1.21 p.p.m. high with 1.0 p.p.m. N as nitrite. Rideal-Stewart and Hale-Melia values are approximately the same as the Winkler value on aerated distilled water.

In the next series of experiments 5 per cent and 10 per cent of sewage were added. The results are given in Table III. It must be remembered that the addition of fresh sewage to aerated distilled water reduces the dissolved oxygen content due to oxygen consumption by micro organisms, hence these results are comparable only in each dilution.

TABLE III.

	Aerated, distilled, H_2O	5 pct. sewage	10 pct. sewage
Levy	8.30	8.27	7.73
Winkler	7.95	7.42	6.78
Rideal-Stewart		7.32	6.81
Hale-Melia		7.25	6.65

In the presence of the organic matter of sewage, the Levy values are still considerably higher than the Winkler or its modifications. The Winkler, Rideal-Stewart and Hale-Melia values are all practically the same. Evidently the organic matter has not destroyed iodine to any extent.

This point was studied further, as follows:

Dissolved oxygen was determined in mixtures of nitrite-free sewage and aerated water; the remaining amount of liquid, containing free iodine, was divided into two portions. One portion was kept exposed to the air in beakers, the other portion was kept in stoppered bottles out of contact with air. The results are given in Table IV.

TABLE IV.

Reduction of iodine by organic matter.

Percent Sewage	0	25	50	75	100
Dissolved Oxygen	8.08	5.16	2.41	.053	0.00
Dissolved Oxygen, in closed bottles after standing 1 week	8.00	4.40	1.54	3.30	0.00
Dissolved Oxygen in beakers	0.00 in 1 wk.	0.00 in 2 da.	0.00 in 1 da.	0.00 in ½ da.	

It would seem from this table that organic matter does not reduce iodine to an appreciable extent under the conditions of the Winkler method, in which the iodine solution is kept in closed bottles until ready for titration, and is exposed to the air but a few minutes during titration.

In the next series of experiments .5 p.p.m. N as nitrite and 5 per cent sewage was added. Then, keeping the nitrite constant, the sewage content was increased to 10 per cent. Results are given in Table V.

TABLE V.

	Aerated, distilled, H_2O	.5 p.p.m. N as nitrite	
		5 pct. sewage	10 pct. sewage
Levy	8.23	7.90	7.60
Winkler	7.55	7.54	6.99
Rideal-Stewart		7.07	6.54
Hale-Melia		7.14	6.47

Finally, 1.0 p.p.m. N as nitrite and 5 per cent sewage was added, then, keeping the nitrite constant, the sewage content was increased to 10 per cent. Results are given in Table VI.

TABLE VI.

	Aerated, distilled, H_2O H_2O	1.0 p.p.m. N as nitrite	
		5 pct. sewage	10 pct. sewage
Levy	8.95	8.50	7.72
Winkler	7.99	8.36	7.28
Rideal-Stewart		8.36	6.76
Hale-Melia		8.41	6.73

Levy values are invariably higher than any of the others; Winkler values are high in the presence of high nitrites; Rideal-Stewart and Hale-Melia agree very well.

The experiments shown in Tables I, II, III, V, and VI have been duplicated, with similar results, but the tables have not been included in this paper. In all, 300 dissolved oxygen determinations were made.

The general conclusions to be derived from this work are:

1. Levy values are higher than Winkler in practically all cases, except where high nitrites are present.

2. Winkler values are much too high in the presence of high nitrites. Either the Hale-Melia or the Rideal-Stewart modification will give correct results up to 1.0 p.p.m. N as nitrite and 10 per cent sewage. The procedure of the Hale-Melia is so much simpler than that of the Rideal-Stewart that it is much preferable for field work.

It is of interest to note that in a large number of comparative determinations of dissolved oxygen on the Illinois State Water Survey[1] were, on the average, 1.0 parts per million higher than results by the Winkler method used by the Sanitary District of Chicago.

The Levy method was used by the New York Metropolitan Sewerage Commission[2] in its work on New York Harbor. The Winkler method was used by Birge and Juday[3] in their extensive work on Wisconsin lakes. Phelps[4] has used the Rideal-Stewart method in his work on the Ohio River. Lederer[5] uses the Hale-Melia method at the Chicago Sanitary District; it is also used by Hale and Melia[6] at the Mt. Prospect Laboratory, Brooklyn, N. Y. Thus it is seen that a standard method is desirable in order that all results may be comparable. To this end the experiments indicate the advisability of discarding the Levy method, and of officially adopting the Winkler method, with the Hale-Melia modification in the presence of high nitrites.

The experimental work reported in this paper was done in the laboratories of the Illinois State Water Survey in July, 1914.

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[1] Unpublished work, Ill. St. Water Survey.
[2] Report, N. Y. Met. Sewerage Comm., 1914.
[3] Wisconsin Survey Bull. XXII, page 11.
[4] Jour. Ind. and Eng. Chem., Aug. 1914, pp. 682.
[5] Jour. Ind. and Eng. Chem., Nov. 1914, pp. 884.
[6] Jour. Ind. and Eng. Chem., Dec. 1913, pp. 976.