

Factors Affecting Dissolved Oxygen Analysis in Beer and Water¹

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ABSTRACT

A number of chemical and instrumental dissolved oxygen techniques were studied for their response to added oxygen as well as to factors other than oxygen (pressure, flow, SO₂, Cl₂, and pH). Polarographic (IL 531, IL 540, IL 545) and galvanic (Hays meter) instruments showed similar increases in output with added oxygen (in beer), but the galvanic instrument gave different absolute values. The difference in absolute values was largely caused by the indigo carmine calibration technique (used to calibrate Hays meters), which responds to species other than dissolved oxygen. Pressure and flow rate had little effect on polarographic instruments, provided the oxygen concentration was below saturation. The Hays meter output decreased with decreasing flow rate. Decreasing the pH of water by the addition of phosphoric acid lowered the apparent oxygen content as assessed by the Winkler and IL 531 methods, whereas the Hays method showed an increase. Chlorine in water caused an apparent oxygen increase with the Hays meter and a decrease with the IL 531 analyzer. Sulfur dioxide in water produced an apparent oxygen increase with the IL 531 analyzer. Calibration of the Hays meter near the low end of its range produced low oxygen results. When an "offset" was introduced in the calibration procedure, the performance of the Hays meter improved. A single offset value was not useful with all Hays meters, as each instrument examined had a somewhat different response to oxygen.

Key words: *Beer, Calibration, Dissolved oxygen, Nonoxygen effects, Water*

The measurement of dissolved oxygen (DO) has long been of interest to brewers in a number of areas of the brewing process (1,2,4-6,8,9). Each area has certain problems. With wort, high levels of oxygen are present and errors can occur if a supersaturation condition exists or if undissolved air or oxygen bubbles are present (8). The DO levels of interest in beer and water are so low that measurement difficulties are encountered. The ASBC has devoted subcommittee work to the accurate measurement of DO in water, wort, and beer (1,2).

Recently, Hahn and Hill (4) compared results obtained with several different kinds of DO measuring instruments: galvanic cell (Hays), Hersch cell, membrane-protected galvanic cell (Rexnord), and membrane-protected polarographic cell (IL 540). Both beer and water samples were used, and the effects of carbonation level, temperature, and changes in DO levels brought about by temperature changes or gas-liquid equilibrium adjustments were studied.

The work reported here compares results obtained with four different instruments, one direct galvanic cell (Hays) and three membrane polarographic probe units (IL 531, IL 540, IL 545), and with two chemical methods, indigo carmine (7) and Winkler (3). The effects of a number of physical and chemical factors were examined. Some of the variables studied by Hahn and Hill were reevaluated using a different experimental approach.

EXPERIMENTAL

Instruments and Calibration Procedures

Three polarographic oxygen analyzers—IL 531, IL 540, and IL 545 (Instrumentation Laboratories, Inc., Lexington, MA)—were used in this study. Air and oxygen-free nitrogen (99.995% purity, from Liquid Carbonic) were employed to establish full-scale and zero settings.

The Hays Oxygen Analyzer, model 625.02 (Hays Corp., Michigan City, IN) was calibrated with two different procedures.

In one case, the oxygen content of beer from a lager tank was measured with the indigo carmine method; the Hays instrument was then connected to this tank and the control was adjusted until the meter displayed the indigo carmine result. The other procedure substituted an IL 545 oxygen measurement for the indigo carmine determination.

Chemical Methods

The Winkler oxygen method (3) was applied to water samples. The indigo carmine determination for dissolved oxygen (7) was used on some beer samples.

Experimental Apparatus

Most laboratory measurements were conducted in a closed loop system such as that shown in Fig. 1. This consisted of a 5-gal Firestone tank, a variable speed pump (Doerr AR59047B781, Doerr Electric Corp., Cedarburg, WI), the DO instruments used in a particular test connected in series, and a septum port from which a sample of liquid could be drawn for chemical analysis. An ice-water bath was used to maintain subambient (1-3°C) temperature when required. In some experiments, a pressure transducer (Validyne model CD12/DP15TL, Validyne Engineering Corp., Northridge, CA) and a platinum resistance thermometer (Instrulab model 4601-41X-03, Instrulab Incorporated, Dayton, OH) were included in the sample loop.

In one experiment, the arrangement in Fig. 2 was used. For this system, liquid flow was produced by a difference in CO₂ pressure between the two tanks. The effect of pressure on the measurements was examined with the apparatus shown in Fig. 3.

In some experiments, the effects of certain gases on the instrument indications were observed. A Brooks Digital Gas Blender (model 5841-1A2ZZ, Brooks Instrument Division, Emerson Electric Co., Hatfield, PA) was used to blend the test gas with nitrogen in desired ratios. Gas flow rates were 0-10 standard cubic centimeters per minute for Channel 1 (test gas) and 0-6000 standard cubic centimeters per minute for Channel 2 (nitrogen). The gas outlets of each channel were connected with a "tee" to produce the final gas mixture, which was bubbled into a beaker of water. An IL 531 probe was immersed into the water to determine the effect of the gas on the electrode response.

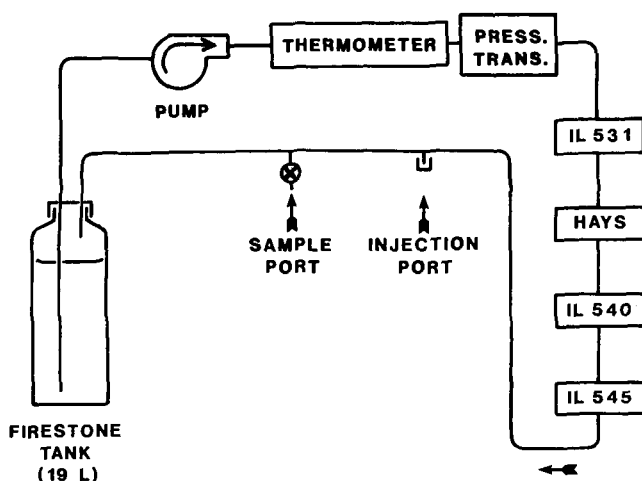


Fig. 1. Experimental arrangement for studying effects of various levels of dissolved oxygen on different instruments.

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RESULTS AND DISCUSSION

Response of Various DO Instruments and Methods to Added Oxygen

In evaluating various methods of measuring DO, the primary interest is in the response of the technique to different oxygen levels. Hahn and Hill (4) approached this in two ways. In the first, the temperature of an equilibrium system was changed, which changed the DO concentration. As the authors noted, this led to problems of interpretation because none of the instruments studied had temperature compensation. Their second approach was more straightforward; changes in gas-liquid equilibrium were produced with the addition of CO₂ of known oxygen content.

We selected a simple approach. All four of the test instruments

TABLE I
Instrument Response to Added Oxygen

Injection	Calculated Cumulative Oxygen Concentration	Apparent Oxygen (mg/L) Measured by			
		IL 531	IL 540	IL 545	Hays
0	0.00	0.04	0.01	0.00	0.24
1	0.025	0.06	0.04	0.03	0.26
2	0.050	0.09	0.06	0.05	0.28
3	0.075	0.11	0.09	0.08	0.31
4	0.100	0.14	0.11	0.10	0.33

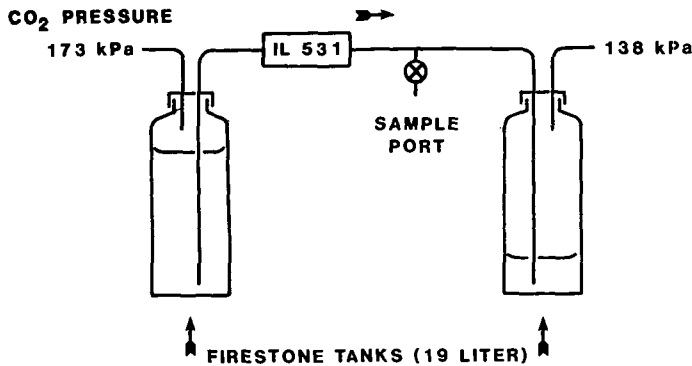


Fig. 2. Experimental arrangement for comparing indigo carmine and IL 531 results.

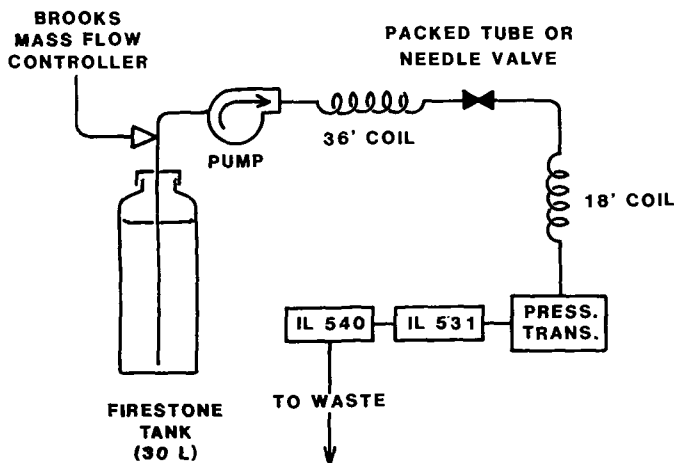


Fig. 3. Experimental arrangement for studying effect of pressure on instrument response.

were connected in series in a closed loop system (Fig. 1). The polarographic instruments were calibrated with air, and the Hays meter was calibrated with the indigo carmine procedure. The reservoir contained approximately 17 L of beer purged with oxygen-free nitrogen and recarbonated with oxygen-free CO₂. Four successive 50-ml injections of air-saturated water (containing 8.5 mg of O₂ per liter) were made, and the response of each instrument was noted after each injection. The results are shown in Table I. Although the starting values were very different, the step changes for each instrument after each water addition were quite similar. The calculated total concentration change was 0.10 mg/L, and the instruments showed a total change of 0.09–0.10 mg/L, in very good agreement with the calculated amount. The results have also been plotted in Fig. 4. Although displaced vertically from one another, the lines are very nearly parallel, showing that in this experiment the oxygen response for all instruments was very nearly the same. Further, the slope of the lines, particularly for the polarographic analyzers, is in near perfect agreement with the calculated addition. The difference between the IL 540 and the IL 545 is one unit on the digital meter and is thus very small. The IL 531 did give a somewhat different intercept.

A second study, performed in the plant and in the laboratory, compared the indigo carmine and IL 531 measurement techniques. Some of the beer used in this experiment (4–7 days in fermentation) contained a large amount of yeast (more than ten million cells per milliliter). The Hays meter was not tested under these conditions because, in our experience, use of the meter in yeasty beer has produced erratic results.

In the laboratory portion of this experiment, the arrangement shown in Fig. 2 was used. The following sequence of operations was performed several times. Beer in a Firestone tank was aerated for 45

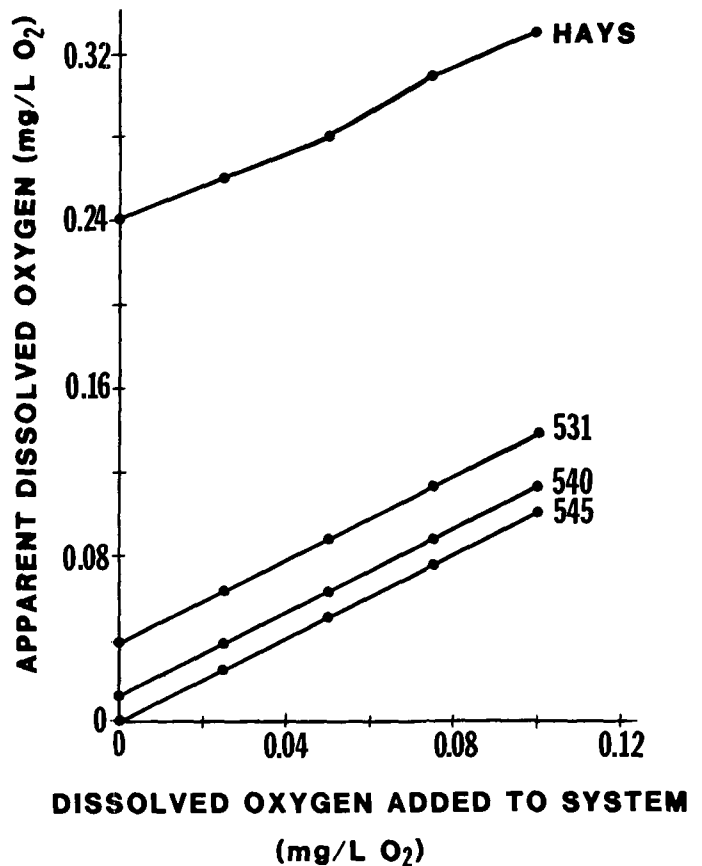


Fig. 4. Comparison of dissolved oxygen results obtained with several different instruments.

sec with a carbonating stone. The beer was mixed and then forced via CO₂ pressure into a second Firestone tank. During the flow from one tank to the other, the IL 531 reading was noted and a sample was then drawn for indigo carmine determination. A total of seven observations were made in this manner. A number of comparisons were also made on samples in the plant. An IL 531 measurement was made on-line and a corresponding sample of the same beer was drawn for indigo carmine analysis. The results are shown in Table II. In every case but one, the oxygen values determined by indigo carmine were higher than those determined by the IL 531. Hahn and Hill also found higher results for filtered beer with the indigo carmine method (4) and attributed them to a reaction of the dye with electron transfer agents other than oxygen. A scatter plot of the data from Table II is shown in Fig. 5. The slope obtained from linear regression, 1.07, suggests, as expected, essentially a one-to-one correspondence of indigo carmine and IL 531 results; the intercept, -0.139 mg/L, shows the degree to which indigo carmine values are higher than the IL 531 results. In our experience, this intercept ranged between -0.12 and -0.14. This value presumably varies in different beers and depends on the concentrations of various substances capable of reacting with the indigo carmine dye.

In a third set of experiments, the IL 531 and the Hays meter were compared using water. The two instruments were placed in series on a sample line coming from the plant's deaerated water system. The IL 531 was calibrated once per week in air, whereas the Hays meter was adjusted once per week to the Winkler-determined oxygen content of the water. Fifteen oxygen measurements of the water were made with the two instruments and the Winkler method over a three-week test period. The results are shown in Fig. 6. In the first week of testing, all three sets of results were roughly parallel, although the Hays meter values were displaced from the other two. During the middle part of the experiment, however, the Hays meter response was often opposite to that of the Winkler-and-IL 531 method, but in the last week it again agreed well with the other two methods. Treating the Winkler method as the independent variable, scatter plots were made (Figs. 7 and 8) and correlation coefficients were calculated. The correlation coefficient for the IL 531 results versus Winkler results was 0.912, whereas for Hays results versus Winkler results it was -0.136. These numbers confirm what is shown in Fig. 6, ie, that the IL and Winkler results correspond well, whereas the Hays and Winkler results are, at times, in poor agreement.

Physical Factors Affecting Oxygen Measurements

A fourth set of experiments was concerned with the effects of pressure and flow rate on the membrane-covered probes (IL 531 and IL 540). The arrangement shown in Fig. 3 was used for these tests, with water as the test medium. In the first test, with air-saturated water in the system, the pressure was increased in steps without adding oxygen. Pressure was applied by increasing the pump speed while maintaining the flow constant at 23 L/hr by adjusting the flow meter needle value on the IL 540. The results (Table III) show that hardly any effect on instrument response was observed over a range of 0-517 kPa (0-75 psig) above atmospheric pressure.

If oxygen levels reach supersaturation, the situation is more complex. In a second test, air was added to the low pressure side of the pump at a fixed rate, while again the system pressure was increased in several steps (Table III). As expected, the addition of air increased the instrument results; however, they change by only 50-80% of the calculated value even at maximum pressure. Increasing the length of tubing before the instruments produced higher values (90-95% of expected). Still better agreement (95%) was obtained when a glass wool plug was placed in the copper tubing; this presumably provided more intimate contact between undissolved gas and liquid.

Rather than dissolving the bubbles, others have approached the problem differently by employing a debubbler to remove entrained

TABLE II
Dissolved Oxygen in Plant and Laboratory Beer Samples

Sample Origin	Oxygen (mg/L) Measured by	
	IL 531	Indigo Carmine
Plant	0.05	0.17
	0.06	0.14
	0.13	0.26
	0.01	0.19
	0.01	0.20
	0.01	0.21
	0.03	0.30
	0.02	0.27
Laboratory	0.00	0.14
	0.02	0.12
	0.05	0.19
	0.10	0.18
	0.25	0.45
	0.76	0.97
	1.05	0.92 ^a

^a May be low because of yeast consumption of O₂.

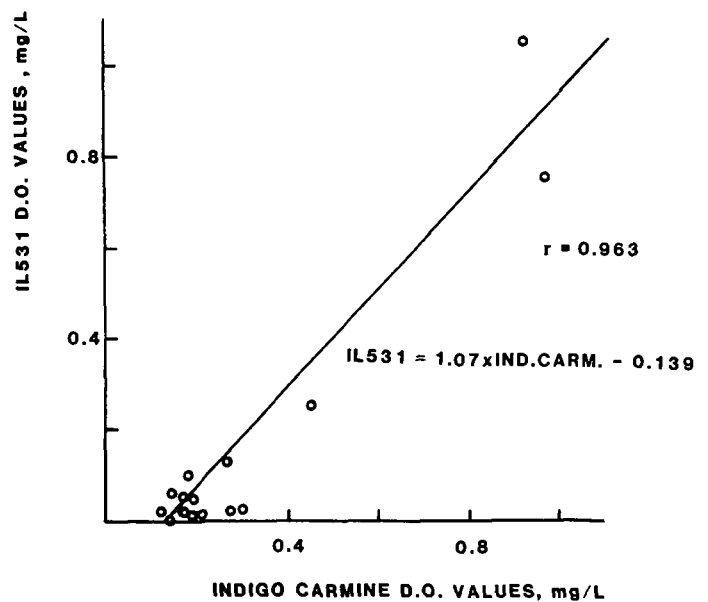


Fig. 5. Comparison of indigo carmine and IL 531 results in beer.

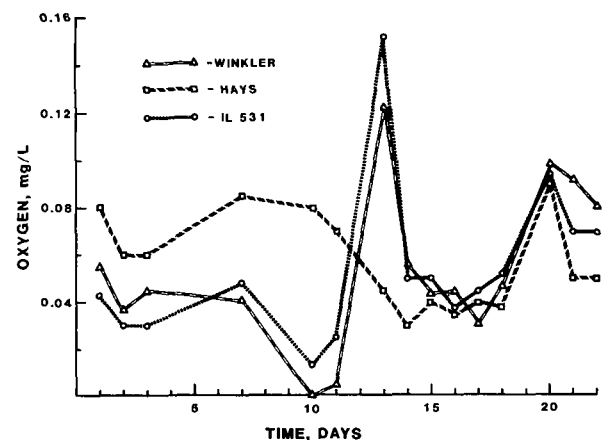


Fig. 6. Oxygen results in blending water obtained from three different methods over a three-week period.

bubbles before measurement (8). This, too, ensures that the probe will be exposed only to DO. Both of these approaches apply principally to wort, in which oxygen levels above saturation occur. If measurement of all of the added oxygen is important, then measurements under pressure must be taken sufficiently far downstream to allow dissolution to occur. The downstream position of the IL 540 in this experiment probably accounts for the higher oxygen values observed with it than with the IL 531.

The effects of flow rate variations on the IL 531 and Hays meter were studied in Experiment 5. Again the arrangement shown in Fig. 1 was used. The effects of three flow rates were tested at five oxygen concentrations. The results are shown in Table IV. The IL 531 showed a flow sensitivity only at the lower oxygen concentration; however, the largest difference was only 0.02 mg/L. The Hays meter results were influenced by flow rate at all concentrations studied. The values observed at 23 L/hr were about 65% of those at 68 L/hr. The flow sensitivity of the Hays meter can be accounted for by the large cathode surface area. A large electrode consumes

large amounts of oxygen, which in turn requires rapid renewal of the liquid at the cathode-liquid interface to keep this layer representative of the bulk liquid. In practical terms, standardization and normal use of the Hays meter should always be done at the same flow rate.

Chemical Factors Affecting Oxygen Measurements

Oxygen measurements made with the IL 531 during the later stages of fermentation showed higher than zero (0.01–0.04 mg/L) oxygen levels. This phenomenon was further investigated (in the sixth experiment) by conducting oxygen measurements on beer fermented in the pilot plant and purged for 24 hr with pure nitrogen. After purging, the IL 531 showed the oxygen content to be 0.03 mg/L. Water purged for 1.5 hr with the same nitrogen showed an oxygen content of 0.01 mg/L. At this point, we considered the idea that substances produced during the course of

TABLE III
Effect of Pressure on the Oxygen Readings Obtained from Polarographic Membrane Probes in Water

Condition ^a	Pressure (kPa) ^b	Oxygen (mg/L) Measured by	
		IL 540	IL 531
No O ₂ added	41	10.1	9.9
	103	10.3	10.1
	172	10.3	10.1
	352	10.4	9.9
	517	10.4	9.8
3.5 mg/L of O ₂ added	41	9.8	9.9
	124	10.4	9.9
	172	11.4	10.8
	352	12.5	11.1
	517	12.7	11.6

^a In the first condition the system contained air-saturated water; in the second, air was introduced to increase the oxygen level by 3.5 mg/L.

^b One kilopascal (kPa) equals 0.145 lb/in.².

TABLE IV
Effect of Sample Flow Rate on IL 531 and Hays Meter Results at Various Oxygen Levels in Water

Flow (L/hr)	Result (mg/L of O ₂) Measured by	
	IL 531	Hays
68	0.51	0.66
45	0.51	0.55
23	0.51	0.43
68	0.39	0.55
45	0.39	0.45
23	0.39	0.34
68	0.29	0.42
45	0.29	0.34
23	0.28	0.27
68	0.16	0.29
45	0.16	0.24
23	0.15	0.19
8	0.14	0.14
68	0.09	0.19
45	0.09	0.16
23	0.08	0.13

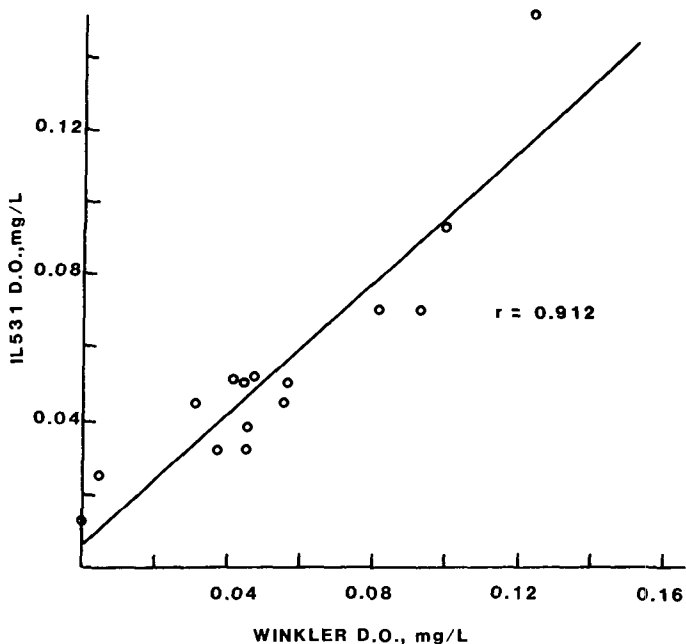


Fig. 7. Scatter plot and linear regression line for Winkler and IL 531 dissolved oxygen results in blending water.

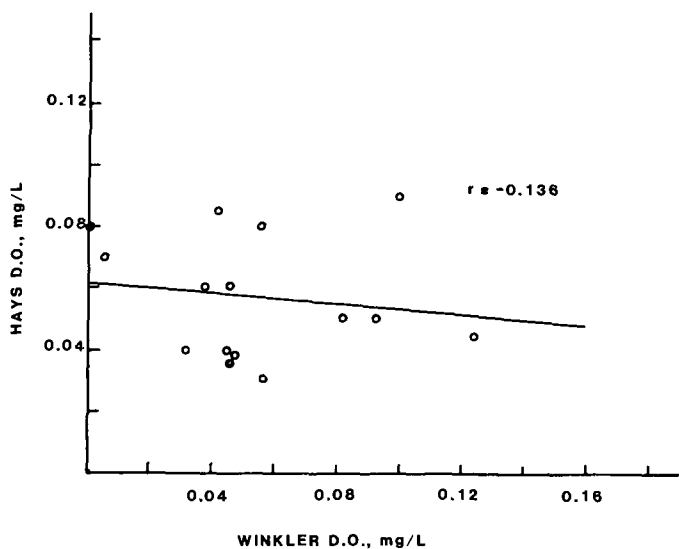


Fig. 8. Scatter plot and linear regression line for Winkler and Hays meter dissolved oxygen results in blending water.

fermentation might affect the IL 531 oxygen reading. Either these would have to be gaseous, in order to pass through the gas-permeable membrane and be detected, or they would have to alter the membrane permeability. The theory that a gas caused the effect seemed much more likely, so several gases that might be produced by yeast (CO, NO, NO₂, and SO₂) were tested. Each of the gases was mixed with pure nitrogen and bubbled into a beaker of distilled water at room temperature. IL 531 oxygen measurements were made while the gas mixtures were bubbling through the water. The results are shown in Table V. Of the four gases tried, SO₂ and NO caused an oxygen response above 0.01 mg/L. Because NO gave a response only at 860 ml/L (v/v) and because nitric oxide concentrations much less than this are expected in fermentation, no further consideration was given to this gas as a possible cause of the apparent oxygen. Sulfur dioxide, however, did cause a response at low concentration. Based on the partial pressure of SO₂ in this experiment (27×10^{-6} atm) and the solubility of SO₂ in water at 22°C (105 mg/L), the equilibrium concentration of SO₂ in the water should be 3 mg/L. Because SO₂ concentrations often reach 3 mg/L or even higher during fermentation, more than enough SO₂ is present to account for all of the apparent oxygen detected by the electrode. At beer pH, 99% of the SO₂ is present as the bisulfite ion, which cannot diffuse across the electrode membrane. This explains why it was not possible to remove the effect with exhaustive nitrogen purging (which would have removed oxygen) and indicates that very tiny amounts of SO₂ diffusing across the electrode membrane cause a large effect. Exposure to large concentrations of SO₂ caused the IL 531 to read off-scale for some time. Fig. 9 shows the response of the IL 531 in pure CO₂ versus time after a 7-min exposure to an SO₂ solution prepared by dissolving 7 g of Na₂S₂O₅ in 250 ml of 3N sulfuric acid. The electrode recovered completely overnight (15 hr). At this pH, virtually all of the SO₂ present is in the gaseous state and can diffuse across the electrode membrane.

The IL 540 and IL 545 have an electrode design that differs from that of the IL 531. Because this configuration always gives a zero indication late in fermentation, it does not appear to be affected by SO₂.

Chlorine is another substance the presence of which in water may influence instrumental oxygen determinations. The effect of added chlorine (as NaClO) on the IL 531 and on the Hays meter was tested in the laboratory. Chlorine concentrations typically found in

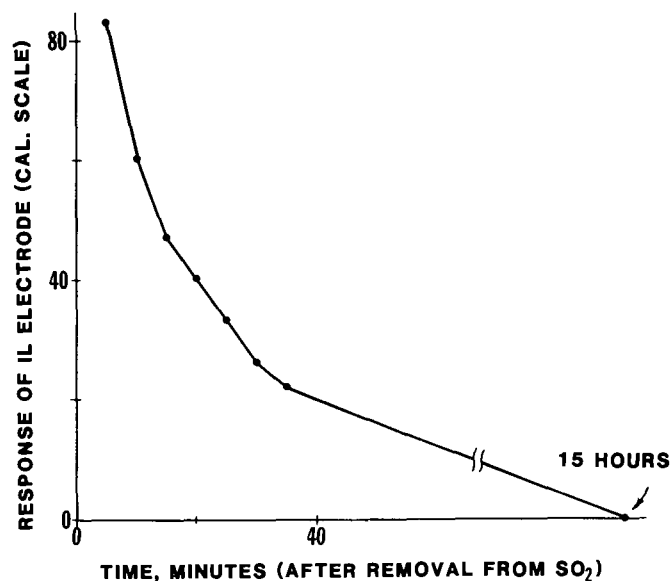


Fig. 9. IL 531 response in pure CO₂ vs time after exposure to an SO₂ solution.

treated water were used. Additions of chlorine affected the outputs of both instruments but in opposite directions (Table VI). The total effect on the IL 531 was relatively small (0.03 mg/L), but this is at variance with the manufacturer's statement² that chlorine concentrations up to 0.5 mg/L have no effect on the instrument. The Hays meter output increased markedly with the addition of chlorine. Because chlorine is an electronegative element, it is likely to be reduced at the cathode, as is oxygen, and would contribute to an apparent oxygen reading. Because the equivalent weight of chlorine is approximately one fourth that of oxygen, the effect would be about one fourth that of the same weight of oxygen. Nevertheless, the presence of chlorine in water can significantly affect the Hays meter output.

The effects of pH (as carbonation level) on the Hays meter and IL 540 have been studied by Hahn and Hill (4), who showed that as the amount of CO₂ in water increased to three volumes per volume of water, the IL 540 output increased only negligibly (by ~ 10 µg/L).

TABLE V
Effects of Dissolved CO, NO, NO₂, and SO₂ on the IL 531 Oxygen Analyzer

Gas	Concentration in N ₂ (µl/L)	Apparent Dissolved Oxygen Concentration (mg/L)
CO	27.4	0.005
	210	0.01
	860	0.01
NO	27.4	0.005
	210	0.005
	860	0.02
NO ₂	27.4	0.005
	210	0.005
	860	0.005
SO ₂	27.4	0.03
	210	0.035 (0.045 after 45 min)

TABLE VI
Effect of NaClO Addition on IL 531 and Hays Meter Readings

Cumulative Amount of Added Cl ₂ (mg/L)	Oxygen (m/L) Measured by	
	IL 531	Hays
0	0.16	0.16
0.24	0.14	0.22
0.48	0.13	0.22
0.72	0.13	0.24

TABLE VII
Effect of pH Change^a on Oxygen Measurements

Cumulative H ₃ PO ₄ Added (ml/35L)	pH	Dissolved Oxygen (mg/L) Measured by		
		IL 531	Hays	Winkler
0	7.5	0.33	0.30	0.29
5	5.6	0.30	0.28	0.27
10	3.2	0.27	0.45	0.19
15	2.8	0.24	0.44	0.15

^a From concentrated H₃PO₄ added to ~35L of H₂O.

² Personal communication.

Under the same conditions, the Hays meter output increased by about 120 $\mu\text{g/L}$. We examined the response of several techniques to the addition of phosphoric acid to water. Table VII contains results comparing the IL 531, Hays meter, and Winkler methods. All three sets of results changed with decreasing pH. As the ASBC Subcommittee on Oxygen has observed (1), low results are obtained with the Winkler procedure if it is not conducted in a sufficiently alkaline medium. The decreasing Winkler results can readily be explained by this fact. The increasing Hays meter results are probably caused by an increase in current passing through the meter. The addition of phosphoric acid decreases the resistance of the measured solution based on the equation $E/R = i$, in which $E =$ volts and $R =$ ohms. This causes an increased current, which results in an apparently higher oxygen content. Presumably, the

ionization of CO_2 in water would cause the same type of apparent oxygen increase as would phosphoric acid. This explanation may also account for the increased Hays readings that occurred with the addition of sodium hypochlorite in the previous experiment, ie, the added ions decreased circuit resistance.

The results indicate that Hays meters will produce erroneous results if the carbonation level at which they are standardized differs significantly from that at which they are used. This problem is probably more pronounced in water, in which the relative change in the number of ions present is greater for a given amount of CO_2 than that in beer.

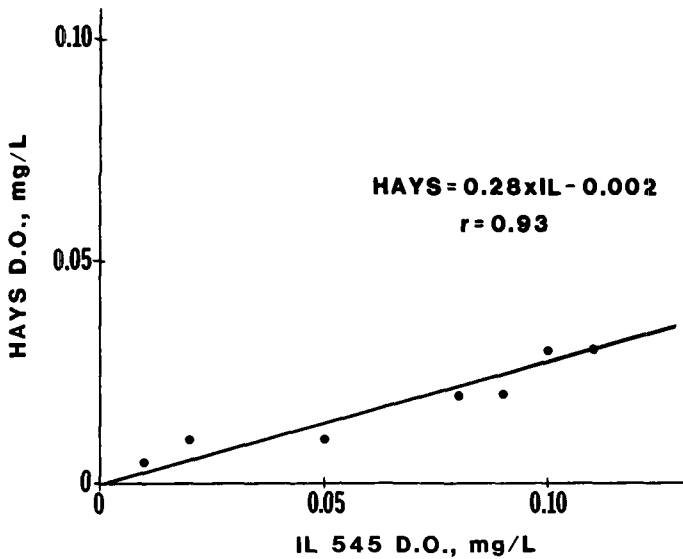


Fig. 10. IL 545 vs Hays meter dissolved oxygen results with a Hays meter offset of 0.1.

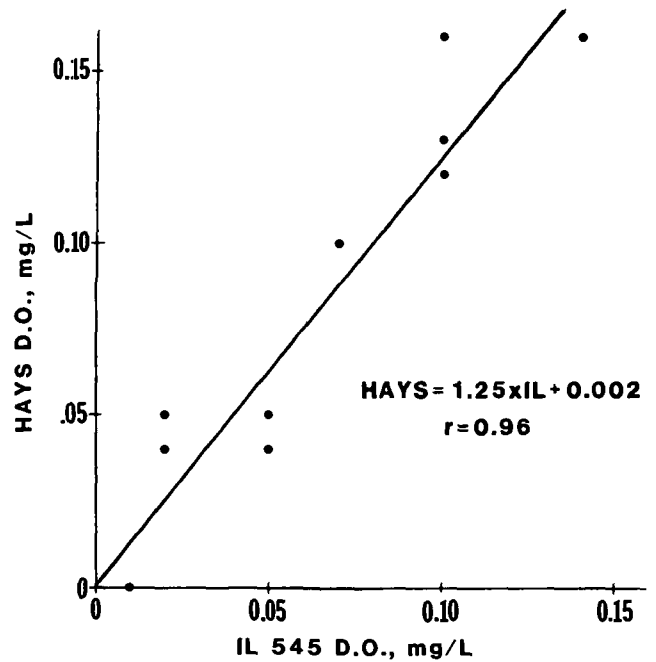


Fig. 12. IL 545 vs Hays meter dissolved oxygen results with a Hays meter offset of 0.5.

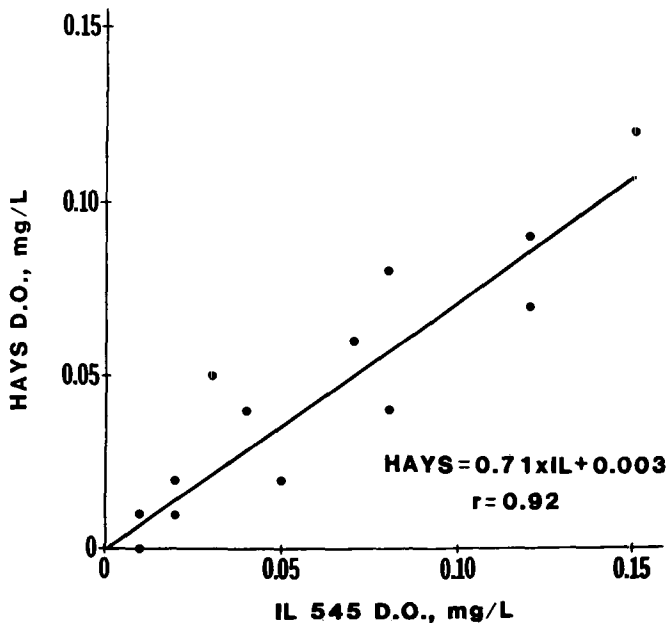


Fig. 11. IL 545 vs Hays meter dissolved oxygen results with a Hays meter offset of 0.3.

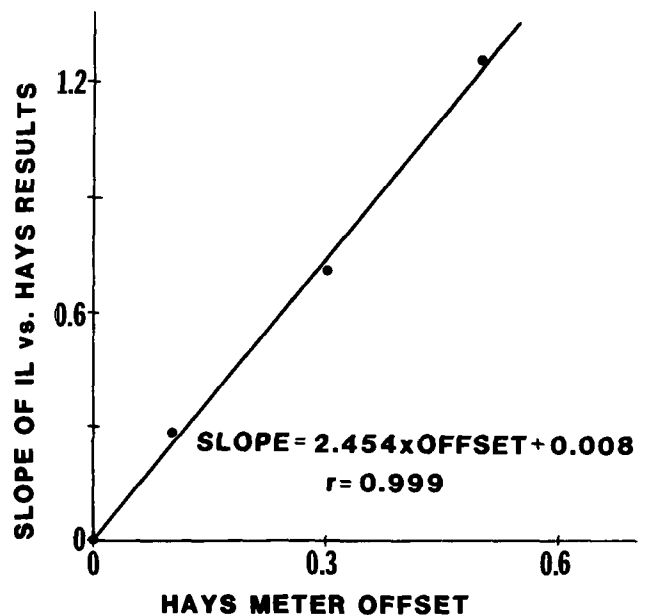


Fig. 13. Hays meter offset vs (slope of IL 545 vs Hays meter results).

The IL 531 results decreased with decreasing pH, which was quite unexpected. No oxygen should be consumed in the system as a result of adding phosphoric acid, nor should the probe membrane be permeable to the acid. Thus, although the results are quite clear, no ready explanation for them is available.

Effects of Calibration on Hays Meter Response

As was shown earlier, Hays meter results for added oxygen in beer were higher than those obtained with other methods. Because of the high results encountered when Hays meters were calibrated via the indigo carmine technique, calibration was attempted with the IL 545 oxygen analyzer. The oxygen content of a single beer tank was determined with the IL 545. The Hays meter was set to indicate this value and then the oxygen content of other tanks was measured with this standardized Hays meter. The Hays meter did not respond to oxygen in some cases in which oxygen should have been detected. Because the set point was low (typically 0.0–0.04 mg/L) and because the Hays performs better when calibrated nearer midscale (as shown in Fig. 4), we reasoned that the Hays meter was insensitive to oxygen when calibrated at low levels. Experiments confirmed this premise. Oxygen concentration in a number of beer storage tanks and lines was measured with both an IL 545 and a Hays meter standardized with an IL 545. In this set of experiments, however, the standard Hays meter reading was offset (ie, increased) by 0.1, 0.3, or 0.5 mg/L. The results are shown in Figs. 10–12. The Hays meter became more sensitive to oxygen as the offset increased. A plot of Hays meter offset versus the slope of the lines from Figs. 10–12 is shown in Fig. 13. In order to obtain a 1:1 correspondence between Hays meter and IL 545 results, a 0.4 offset would have to be used.

The requirement of a 0.4 offset for the Hays meter also explains the poor results for the Hays meter-Winkler comparison (Fig. 8). Because the Hays meter was calibrated at the low end of its range, it showed little response to changes in oxygen content. This, of course, was confirmed by the low correlation coefficient. The same influence can be seen in the data of Hahn and Hill. In their study of response to oxygen in water, the Hays meter was calibrated on the high side of the range (it indicated 0.12 mg/L at a calculated 0.04 mg/L) and had a higher than theoretical response slope. When the same experiment was done in beer, the Hays meter was calibrated at a lower point (0.05 mg/L at a calculated 0.04 mg/L), and the response slope was lower than theoretical.

Unfortunately, a 0.4 offset cannot be used uniformly for all Hays meters; further testing has shown different Hays meters to require different offsets to maintain a 1:1 correspondence with the IL 545. These results imply that in a typical brewery with several Hays meters, they can be used to detect changes but that unless rigorous calibration checks are made for each meter, they should not be used to indicate absolute oxygen levels.

One further point with respect to the use of Hays meters should be made. Hahn and Hill (4) suggested that highly specific oxygen measurements should be made with membrane polarographic probe or Hersch cell instruments, and we certainly agree. They further noted that in some cases being nonspecific and measuring

oxygen plus other oxidizing substances might be desirable; for this purpose they suggested using a Hays meter with indigo carmine calibration. We found that during lager storage, Hays meter and IL 531 results tended to show similar decreases in oxygen content, whereas the indigo carmine results remained above the other two. Thus, even though the Hays meter may have been calibrated with the indigo carmine technique, the tendency for Hays meter and IL 531 results to parallel one another (Fig. 4) suggests that the Hays meter responds (as does the IL 531) to DO and not to other oxidizing substances. It is presumably incapable, therefore, of assessing the quantity of nonoxygen oxidizing substances.

CONCLUSION

The results discussed above indicate that each of the DO methods available to the brewing chemist has its limitations. The Winkler method can only be applied to water, and interferences (eg, low pH and the presence of oxidizing or reducing substances) must be considered. The indigo carmine technique has been traditionally applied to beer and wort; however, it measures not only DO but other oxidizing substances as well. Overestimates of oxygen as high as 0.14 mg/L can occur when this method is used.

The Hays meter output is too low at low flow rates due to the high rate of oxygen consumption of the electrode. The presence of chlorine causes an erroneously high oxygen indication by the Hays instrument, as does low pH. The magnitude of the calibration has a significant effect on instrument output. At low calibration set points, Hays results are too low, whereas at high calibration levels, the results are too high.

Polarographic membrane probe oxygen analyzers respond well to DO. Chemical interferences are much less of a problem than they are with the Hays meter, although the IL 531 gives a slightly low indication when chlorine is present in water samples and a slightly high indication caused by SO₂ in fermenting wort. The IL 540/545 is not affected by SO₂ under the same conditions.

In summary, as with any analytical technique, methods discussed here should be applied with the knowledge of their limitations.

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