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THE GALVANIC CELL OXYGEN ANALYSER VS.

THE WINKLER METHOD FOR OXYGEN DETERMINATIONS

IN PAPER MILL WASTES

FOR: SENIOR THESIS 470 + 471

BY: EDWIN J. GROSSENBACHER

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THE WINKLER METHOD FOR OXYGEN DETERMINATIONS
IN PAPER MILL WASTES

INTRODUCTION

This study was designed to verify the assumption that the galvanic cell oxygen analyser can be used as a substitute for the Winkler method in determining the dissolved oxygen content of paper mill effluent. The purpose also includes an attempt to show that dissolved oxygen determinations made by either the Winkler method or by the galvanic cell oxygen analyser are of the same magnitude and can be compared directly. The assumption that this is possible has been based upon extensive tests on solutions containing various spent sulfite liquor wastes at various concentrations. These tests show that the electrode measurements are actually a better indication of oxygen content than the Winkler method, at least at high concentrations of the spent sulfite liquors.

An attempt was made in this study to show that little or no deviation is involved between the Winkler and electrode measurements involving paper mill wastes, and thus the above mentioned substitution can be made with the galvanic cell.

LITERATURE SEARCH AND ANALYSIS

For several years, the galvanic cell oxygen analyser has been used

in the determination of dissolved oxygen in pulp and paper mill wastes. However, most tests given this instrument to verify its validity have been in the pulp field with waste effluents containing high concentrations of spent sulfite cooking liquors.

The purpose of this study is to validate the assumption that what holds true with pulp mill wastes, with respect to the determination of dissolved oxygen with the galvanic cell, is also true of paper mill wastes.

A fast, accurate, and simple method of making the dissolved oxygen measurement is needed and the galvanic cell has been accepted as a substitute for the Winkler method based upon the above mentioned assumption.

In a literature search, it was found that very little published data exists on the galvanic cells for use as oxygen analysers. The National Council for Stream Improvement (1) was found to have done the most extensive research in this field in proving the validity of the readings of the galvanic cell. However, once again, most of their work was done with samples containing quantities of spent sulfite liquors (SSL). They had found that the electrode measurements in waters containing spent sulfite liquors indicated a response to the levels of oxygen in excess of those indicated by the Winkler method. At the Northeast Research Center at Tufts University, Medford, Massachusetts in 1963, they undertook to determine the exact affect of sulfite waste liquor on the Winkler test and to determine if the electrode measurement was accurate. The electrode used by the Research Center was a commercial electrode, but the make was not given.

In order to do this determination, it was necessary to develop an absolute method for the determination of dissolved oxygen in solution. For

this a modified Van Slyke gasometric method was investigated. This method involves removal of all gases at near absolute vacuum, then transfer of these gases to a separate container or reaction vessel. The oxygen is then absorbed and reacted with potassium iodide. This procedure, in effect, eliminates the effect of impurities. With several refinements, their procedure was improved to where 99 percent of the oxygen in solution could be stripped, transferred, reacted and measured.

The correlation between the Winkler and the gasometric method showed coefficients of plus 0.995 for distilled water and plus 0.998 for artificial sea water.

The gasometric, electrode, and Winkler methods were used to measure the dissolved oxygen concentrations of the solutions of various concentrations of sulfite suspended solids to determine the correlation of the three methods. In general, the electrode measurement agreed well with the gasometric analysis while the Winkler determination showed increased deviation with increased SSL concentrations. Another observation made was that for a given SSL concentration, regardless of the oxygen level in the solution, the difference between the Winkler reading and the electrode reading remained essentially constant.

The first appreciable deviation in the Winkler test showed at an SSL concentration of 100 ppm of 10 percent SSL. At an SSL concentration of 5850 ppm of 10 percent SSL, the Winkler test showed a maximum deviation, showing no dissolved oxygen in a solution saturated with dissolved oxygen.

They also noted that at higher concentrations of spent sulfite liquor, the electrode began showing a slight deviation from the gasometric method. They

found this deviation to be the result of slight errors incorporated in calibrating the electrode. One such error is the change in solubility of oxygen with increased dissolved solids content.

T. A. Pascoe (2), at present an instructor at Western Michigan University, has also done extensive work with a galvanic cell as an oxygen analyser. His objective was to compare the electrometric measuring methods with the Winkler method on different SSL-varying SSL solids present. His choice of units was the Beckman instrument, his choice being strengthened by the National Council for Stream Improvement, Bulletin No. 159 published in TAPPI, the January 1963 issue.

Dr. Pascoe carried out parallel dissolved oxygen measurements using the Azide Modification of the Winkler Chemical Method and the Beckman Model 777 oxygen analyser. His tests were run on nine liquor samples provided by five mills. He used each sample for dilution to 20 to 2000 ppm of liquor solids.

He found the Beckman instrument to be a simple to operate, rapid, stable device for measuring dissolved oxygen.

In his conclusions, he found that below 20 ppm of liquor solids, the error of the Winkler method is small being in the order of a few tenths of a part per million. Above this level, his findings compared quite favorably with those of the National Council for Stream Improvement.

The National Council for Stream Improvement (3) has published in TAPPI an excellent survey of different instruments for measuring oxygen. They also note that it is possible to plot the sensitivity vs. temperature calibration which theoretically varies logarithmically with the reciprocal of the

absolute temperature.

In connection with the galvanic cell as an oxygen analyser, Vincent F. Felicetta and Donald R. Kendall (4) used a commercial electrode when developing the "Rapid Permanganate" modification of the Winkler test. This modification of the Winkler method was developed to minimize interference by spent sulfite liquors by conducting the oxygen fixation step rapidly and by making a correction for iodine consuming substances on a duplicate sample of water. The commercial electrode was used as a referee method in making the analysis of the modification which they developed, and they accepted the electrode as a reliable means of determining oxygen concentrations.

In exploring for a means of correcting the Winkler calculations made in the presence of SSL to give a true dissolved oxygen measurement, Mulford C. Baker (5) also used a galvanic cell oxygen analyser as a standard to which corrected Winkler results could be compared.

In analysing that material which has been found concerning the validity of the galvanic cell determinations, little can be found concerning application to paper mill wastes. All information seems to point to the fact that spent cooking liquors at high concentrations will cause an error in the ~~the~~ Winkler method. However, these liquors are not normally present in paper mill wastes and thus cannot contribute to erroneous results with the Winkler method on standard paper mill wastes without cooking liquors present.

From the information found, the galvanic cell is not affected by high solids, thus a comparison of the Winkler and galvanic cell determinations on paper mill wastes should give enough information to justify a decision as to whether or not the galvanic cell can be used in place of the Winkler method

and still obtain results comparable to those that would be obtained by the Winkler determination.

EXPERIMENTAL METHODS AND EQUIPMENT

Two commercial electrodes were employed in this study. Both were quick and simple to operate, portable models which could be used either in the lab or in the field.

One of the units employed was the Precision Scientific Galvanic Cell Oxygen Analyser which is a completely self-contained instrument. It is designed with the facility for reading the temperature of the solution to be tested and this temperature reading along with the oxygen reading from the dial can be plotted on a chart giving the corrected dissolved oxygen reading in parts per million. Calibration is required only once per day under normal circumstances and is easily done by comparison with a solution of known oxygen content. This was done in this study by calibrating the instrument against a sample of aerated distilled water which had been allowed to set for five hours to insure a reading of only dissolved oxygen and not suspended oxygen. The known oxygen content is found by use of the Winkler method on a portion of the sample and the instrument set, with the probe in the other portion, to the value obtained from the Winkler method. If the sample is not at 20°C, a temperature correction must be made on the Winkler value before setting the galvanic cell. To compare with the Winkler determinations, all values obtained with the electrode must be corrected to 20°C.

The probe, which is the heart of the unit consists of a ring-shaped lead anode surrounding a silver cathode in an epoxy plastic housing. This results in a durable non-absorbent acid resisting and high dielectric strength

assembly which produces its own precise current. The silver and lead electrodes are first covered by a thin electrolyte pad saturated with electrolyte and covered by a permeable membrane to form a cell capable of maximum current production and high accuracy. The construction also allows accurate readings with a flow rate of only one foot per second past the probe. In the laboratory, hand action can readily accomplish this or it can be accomplished by use of a magnetic stirrer.

The response time of the probe is about one minute and accurate to ± 0.1 ppm oxygen from 5° to 35° C. The probe is designed for use in B.O.D. bottles and for this study, a magnetic stirrer was utilized with the B.O.D. bottles to attain the prescribed conditions.

The accuracy of the thermistor probe for temperature measurement is $\pm 0.1^{\circ}$ C.

The second unit being used in this study is made by the Yellow Springs Instrument Co., Inc., and referred to as the YSI Model 51 Oxygen Meter. This unit also is a completely self-contained, portable unit designed for laboratory and field work.

The YSI oxygen probe is a polarographic system. The cathode is a gold ring embedded in a lucite block. The anode is a silver coil recessed in a central well. The interior is filled with an aqueous solution of potassium chloride. A thin Teflon membrane stretched across the end of the sensor isolates the sensor elements from the surrounding environment. This Teflon membrane is permeable to gases and allows them to enter the interior of the sensor. When a suitable polarizing voltage is applied across the cell, oxygen will react at the cathode causing a current to flow through the cell. The amount of this

flowing through the cell is proportional to the amount of oxygen to which the membrane is exposed. The sensor actually measures the oxygen pressure. Since the oxygen is consumed at the cathode, it can be assumed that the oxygen pressure inside the membrane is zero (this is nearly so at the gold cathode). Therefore, it can be seen that the force causing oxygen to diffuse through the membrane is proportional to the absolute pressure of oxygen outside the membrane. If the oxygen pressure increases more oxygen diffuses through the membrane and more current flows through the cell. A lower pressure in turn results in less current. The membrane diffusion is directly proportional to pressure and the oxygen-cell current relationship obeys stoichometric laws, thus a linear relationship exists between external oxygen pressure and cell current.

Temperature control is as important with this unit because the membrane permeability varies with temperature and changes at a rate of about 4% per $^{\circ}\text{C}$, depending upon the membrane material.

The oxygen probe is responsive to oxygen pressure. Thus, if a container of water is at the same temperature as the air above it and the water is saturated with the air, the oxygen probe will produce the same current whether immersed in the water or exposed to the air above the water. The two currents will be the same at any temperature for a system where the water is saturated with the air above it. Using this characteristic of the sensor, the calibration of the instrument can be effected by taking a reading with the probe exposed to the atmosphere and setting the indicator to a known value for the existing temperature and pressure. In order to eliminate the need for a correction for pressure, the alternate calibration technique was used for this study, that is calibration using distilled water and the Winkler method in the same manner as

with the Precision Scientific unit.

The accuracy, response time, and temperature range and compensation for the YSI Model 51 is very similar to the Precision Scientific unit. With the YSI instrument, temperature compensation is done with a thermistor probe in the same manner.

The factory specified operating procedures for both analysers were followed closely and all measurements were corrected to 20°C. Unfortunately, the units were not available at the same time, therefore, testing with the two instruments was done on different samples.

The Winkler procedure was carried out as follows:

1. The stopper is removed from the B.O.D. bottles.
2. Two ml. of manganous sulfate solution is added to each bottle (keeping the pipette below the surface of the liquid).
3. Two ml. of alkaline iodide solution is added (keeping the pipette below the surface of the liquid) replacing the stopper of each bottle as soon as this solution is added.
4. The bottles are then rinsed and mixed by inverting 10 times.
5. It is allowed to stand until the precipitate settles to the half way point of the bottle.
6. Mixing is again done by inverting 10 times.
7. The precipitate is allowed to settle to the half way point again. To those bottles that do not show a completely white precipitate, add two ml. of concentrated H_2SO_4 .
8. Rinse the bottles and mix by inverting until the floc disappears.
9. Titrate 200 ml. of the sample in a 250 ml. beaker. Add the sodium thiosulfate (0.025N) stirring continuously until the solution reaches a pale straw color. Add an indicator (Thyodene powder was used) and titrate dropwise until one drop destroys the last trace of the blue color.
10. Record the no. of ml. of thiosulfate used as PPM dissolved oxygen in the sample.

All samples tested included only paper machine wastes. Samples were obtained of paper machine wastes from three mills. None of the samples exhibited chlorine present, therefore no correction for chlorine was necessary.

Once again, the samples were diluted with aerated distilled water after having been aerated themselves. Then they were allowed to set five hours before being tested.

RESULTS

WINKLER TITRATION VS.
PRECISION SCIENTIFIC GALVANIC CELL OXYGEN ANALYSER

TABLE I.
MILL A SAMPLE.

<u>Solids (PPM)</u>	<u>a)Winkler DO (PPM)</u>	<u>b)Electrode DO (PPM)</u>	<u>Difference in DO (PPM) = b-a</u>
H ₂ O	7.85	7.85	.00
20	7.85	7.85	.00
60	7.90	7.85	-.05
100	7.75	7.75	.00
200	7.70	7.75	+.05
600	7.75	7.80	+.05
1000	7.65	7.65	.00
1500	7.70	7.75	.00

TABLE II
MILL B SAMPLE

<u>Solids (PPM)</u>	<u>a)Winkler DO (PPM)</u>	<u>b)Electrode DO (PPM)</u>	<u>Difference in DO (PPM)= b-a</u>
H ₂ O	7.35	7.35	.00
20	7.40	7.35	-.05
60	7.50	7.50	.00
100	7.45	7.45	.00
200	7.35	7.40	+.05
600	7.30	7.35	+.05
1000	7.35	7.35	.00
2000	7.30	7.35	+.05

TABLE III
MILL C SAMPLE

<u>Solids (PPM)</u>	<u>a)Winkler DO (PPM)</u>	<u>b)Electrode DO (PPM)</u>	<u>Difference in DO (PPM)= b-a</u>
H ₂ O	7.50	7.45	-.05
20	7.45	7.45	.00
60	7.50	7.50	.00
100	7.40	7.50	+.10
200	7.45	7.45	.00
600	7.40	7.45	+.05
1000	7.40	7.40	.00
1500	7.35	7.40	+.05

WINKLER TITRATION VS.
YELLOW SPRINGS MODEL 51 OXYGEN ANALYSER

TABLE IV

MILL A SAMPLE

<u>Solids (PPM)</u>	<u>a)Winkler DO (PPM)</u>	<u>b)Electrode DO(PPM)</u>	<u>Difference in DO(PPM)= b-a</u>
H ₂ O	7.60	7.65	+0.05
20	7.60	7.65	+0.05
60	7.65	7.60	-0.05
100	7.55	7.55	.00
200	7.50	7.50	.00
600	7.60	7.65	+0.05
1000	7.60	7.55	-0.05
1500	7.55	7.55	.00

TABLE V

MILL B SAMPLE

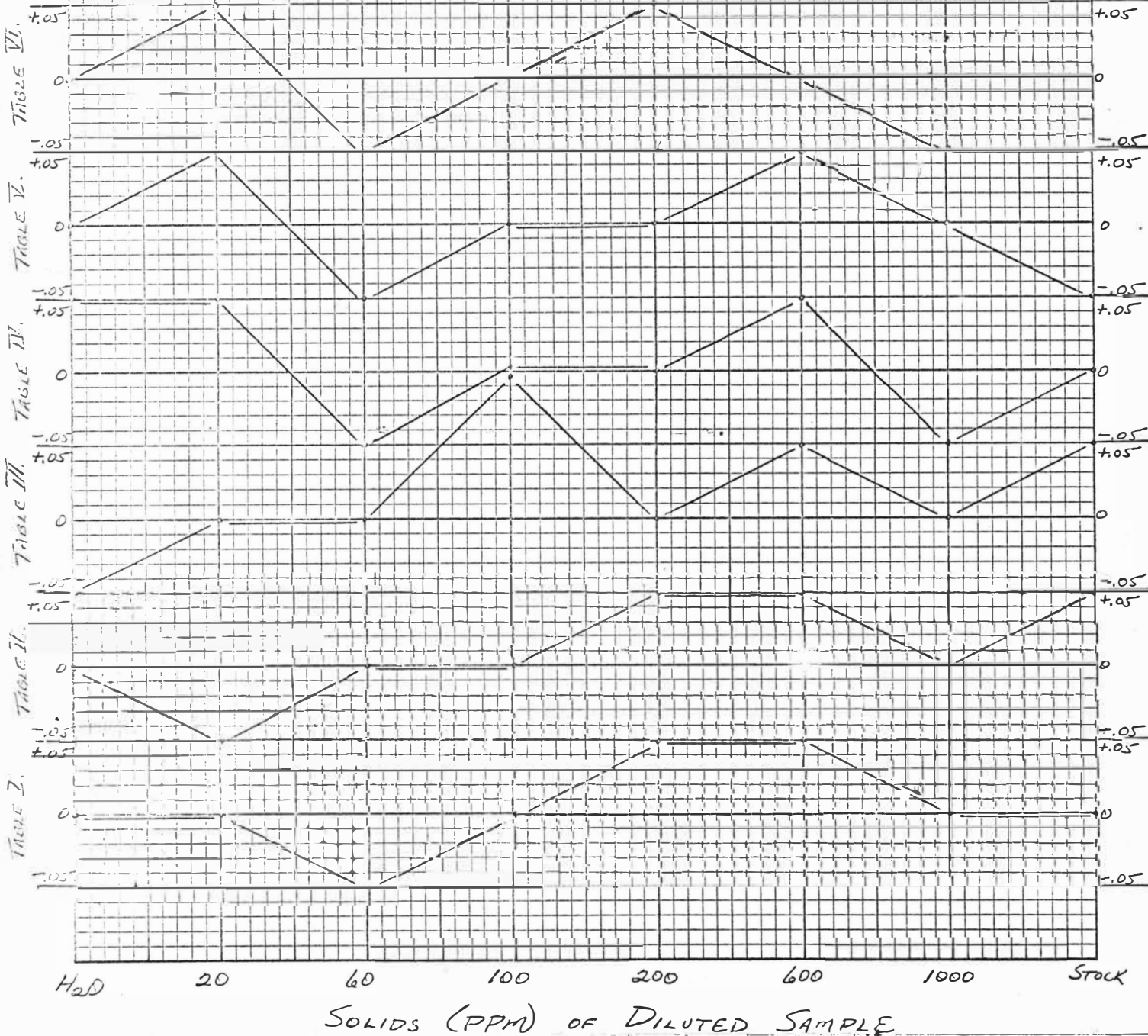
<u>Solids (PPM)</u>	<u>a)Winkler DO (PPM)</u>	<u>b)Electrode DO(PPM)</u>	<u>Difference in DO(PPM)= b-a</u>
H ₂ O	7.55	7.55	.00
20	7.60	7.65	+0.05
60	7.55	7.50	-0.05
100	7.45	7.45	.00
200	7.50	7.50	.00
600	7.50	7.55	+0.05
1000	7.60	7.60	.00
2000	7.70	7.65	-0.05

TABLE VI

MILL C SAMPLE

<u>Solids(PPM)</u>	<u>a)Winkler DO(PPM)</u>	<u>b)Electrode DO(PPM)</u>	<u>Difference in DO(PPM)= b-a</u>
H ₂ O	7.80	7.80	.00
20	7.75	7.80	+.05
50	7.80	7.75	-.05
100	7.70	7.70	.00
200	7.60	7.65	+.05
600	7.65	7.65	.00
1000	7.70	7.65	-.05
1500	7.75	7.70	-.05

(ELECTRODE DO WINKLER DO)



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DISCUSSION OF RESULTS:

In looking over the data compiled in the tables and plotted on the chart, two items appear to be evident. First, it can be seen that the two methods of determining dissolved oxygen, that is, the Winkler method and the electrode method, each appears to agree with the other quite favorably. Secondly, the determinations by the Winkler method fall within the accuracy of the electrode determinations (± 0.1 PPM), and the electrode determinations, in turn, fall well within the accuracy of the Winkler method.

SUMMARY AND CONCLUSIONS

In this study, three mill wastes were analysed by two methods; the Winkler method and the electrode method. In turn, two differing units were used for the electrode method. The objective of this study was to find if the oxygen measurements taken with an electrode would correspond to measurements by the Winkler method on the same samples.

In discussing the results, it can be seen that this objective has been achieved, thus supplying a quick, simple, and reliable means of measurement of dissolved oxygen without going through the Winkler procedure, even at high solids content of waste effluents.

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