ORO-592

# A DISSOLVED OXYGEN ANALYZER

Final Report

By
Arthur S. Gillespie, Jr.
Harold G. Richter

December 31, 1963

Research Triangle Inst.
Durham, North Carolina

UNITED STATES ATOMIC ENERGY COMMISSION • DIVISION OF TECHNICAL INFORMATION

ORO-592
ISOTOPES—INDUSTRIAL TECHNOLOGY
(TID-4500, 37th Ed.)

# A DISSOLVED OXYGEN ANALYZER

This work performed for

The Division of Isotopes Development
United States Atomic Energy Commission

Task No. 11
Contract No. AT-(40-1)-2513

Final Report

by

Measurement and Controls Laboratory
Research Triangle Institute
Durham, North Carolina

Written by

Arthur S. Gillespie, Jr. and Harold G. Richter

December 31, 1963

# LEGAL NOTICE



Printed in USA. Price $2.00. Available from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U. S. Department of Commerce, Springfield, Va.

Other issues of this report may bear the number RTI-2513-T11.

USAEC Division of Technical Information Extension, Oak Ridge, Tennessee

## Abstract

Based on the principle of radio release analysis, an instrument to determine dissolved oxygen in sea water, drinking water and water samples from streams and ponds has been constructed. The dissolved oxygen in the sample reacts with $Tl^{204}$ metal in the instrument thereupon releasing a stoichiometric quantity of Tl-$Tl^{204}$ ion whose activity is measured in a liquid flow beta counter.

The instrument is portable and battery operated for field operations. It is not significantly affected by most dissolved salts and some common oxidizing agents above pH 5. The response is linear (a direct function of oxygen concentration) and with a specific activity of 2 millicuries $Tl^{204}$ per gram of thallium, oxygen concentrations above 0.2 PPM are easily measured. Precision at the 1 PPM level is about $\pm$ 5%, which can be improved by using higher specific activity thallium$^{204}$.

# A DISSOLVED OXYGEN ANALYZER

## I. Introduction

The quantitative determination of small quantities of oxygen dissolved in water is one of the more difficult analytical problems. Dissolved oxygen is of particular interest in the study and prevention of corrosion and in biological studies relating life processes to oxygen concentrations.

Two instrumental techniques for analysis of dissolved oxygen are in use today, neither of which is completely satisfactory. One uses the polarograph reduction of dissolved oxygen at a platinum electrode as a measure of oxygen concentration. Commercial versions using this technique are available from several manufacturers.

This kind of dissolved oxygen analyzer has several disadvantages; the main being its temperature sensitivity, its tendency to drift, and the fact that it measures oxygen tension in the solution rather than dissolved oxygen concentration.

The second method is based on rapid oxidation of thallium metal by aqueous oxygen. Oxidation to the thallous state takes place quantitatively at as low a concentration of dissolved oxygen as can be measured by available techniques. The conductivity of the thallium metal column effluent stream compared with the conductivity of the influent stream is a measure of the oxygen concentration. Several commercial instruments based on this technique are available. One disadvantage of this thallium technique is that ionized substances in the water diminish its sensitivity. Deionizing columns before the inlet conductivity cell do help, but waters containing appreciable quantities of dissolved salts soon saturate the deionizing columns.

A radiometric technique for determining the dissolved oxygen concentration of both pure and natural waters was developed by this laboratory under a contract with

the Division of Isotopes Development of the Atomic Energy Commission[1,2]. It was based on the quantitative oxidation of thallium metal containing $Tl^{204}$ by aqueous dissolved oxygen. The analyzer consisted of a column of thallium - $Tl^{204}$ metal, ($Tl^{204}$ half life 3.6 years, 0.75 Mev beta, $\approx$ 2% EC) deposited on copper turnings, below which was a flow-type Geiger-Mueller tube. Water containing the dissolved oxygen passed through the Tl-$Tl^{204}$ column whereupon $Tl^{+}$ ions formed. The $Tl^{204}$, released at the same time, was detected with a Geiger-Mueller tube and the counting rate was a direct measure of the dissolved oxygen concentration.

The characteristics of this technique of oxygen analysis were studied in enough detail to warrant further investigation of the reaction. The minor and reproducible interference from dissolved salts, operation at pH above 5, low concentrations of oxidizing agents likely to be found in natural waters, and lack of temperature effects were desirable attributes of the technique and are an improvement over other techniques. In addition the inherent sensitivity of the radiometric method (calculated - 1 part oxygen in $10^{12}$ parts water) was sufficient to justify construction of a portable field oxygen analyzer. Such an analyzer would have applications in field situations where other oxygen measuring devices might not be useful. Following is a report of the development and construction of a $Tl^{204}$ radiometric oxygen analyzer and some of its characteristics.

## II. Design of the Oxygen Monitor

In principle, overall design of the oxygen analyzer is simple. Several details were incorporated in the design, however, which improve its performance. These will be described in the next section.

---

[1] Harold G. Richter and Arthur S. Gillespie, Jr. ORO-483 (October 23, 1961), "Investigation of a Radioactivity Technique for the Determination of Dissolved Oxygen".

[2] H. G. Richter and A. S. Gillespie, Jr., Anal. Chem. 34, 1116-19 (1962).

The analyzer consists of two sample inlet ports leading to a thallium column of Teflon. Two inlets are provided--one with an NPT nipple for connecting directly to a process stream and one with a stainless steel standard taper joint to which a "grab" sample can be connected. The sample enters at the bottom of the thallium column and flows upward through it in order to minimize entrapment of air in the thallium interstices. Immediately above the Teflon column is a Teflon-lined counting cell containing two "pancake" beta counters facing each other. Effluent from the counting cell can be passed through an ion exchange column (to remove the $Tl^{204}$ before returning the sample to the environment) or directly to waste.

The analyzer was designed so that only a small volume of sample would be required. This is desirable, not only so that limited samples could be measured, but also to conserve the thallium metal and to permit rapid flushing of one sample from the system before introduction of a second. This necessitated minimum diameter piping and the design of a small volume beta-counting cell.

Calibration of the analyzer is performed in the field by saturating a distilled water sample with air and passing it through the instrument. Atmospheric pressure is read from an aneroid barometer attached to the instrument case and water temperature by means of a thermometer and appropriate tables or curves. With these two pieces of data, the concentration of oxygen in the pure water is known and the instrument may thereby be calibrated.

The electronics of the instrument are transistorized and battery powered.

## III. Construction Details

### 1) Materials of Construction

Teflon is used throughout the instrument for transport of the water samples. This material is used both for its inertness and because it does not readily adsorb radioactivity. Previous work in this laboratory has shown that both Tygon

tubing and polyethylene tubing become contaminated after solutions of isotopes have passed through them. Decontamination of these materials was found to be difficult, whereas Teflon is much easier to decontaminate.

The sample is first placed in the rubber sample bulb which contains a stainless steel standard taper fitting at its outlet. This fitting connects with the standard taper fitting (on the analyzer) which is in turn connected to the Teflon tubing which leads the water sample through the instrument. The rubber sample bulb (actually a medical oxygen rebreathing bag) is used since this is the most convenient method of introducing a sample to the instrument without having to expose it to the ambinet air. As the sample flows from the stoppered rubber container, the latter collapses and thus makes unnecessary any provisions for pressure equalization throughout the analyzer piping.

2) The Thallium Column

The thallium column is made of Teflon in such a way that it can be removed from the counting cell without exposing the thallium to air. The column was designed with the thought that it can be removed easily from the instrument for recharging with metal or for replacing with another column containing thallium of different specific activity. Figures 1-3 give the construction details.

The joints at the top and bottom are compression seals, by means of threaded metal rods (Part 6 of Figure 1) rather than by threads in the Teflon itself. The joints are therefore tighter and leakage of liquid outward, or oxygen inward, is thus avoided.

Parts 3 and 4 on Figure 1 are caps which are placed over the inlet and outlet of the thallium column whenever the cell is removed from the instrument for any reason. They prevent loss of radioactive water from the column and prevent entrance of oxygen. They are used if the column is to be shipped from one place to another.

3) The Counting Cell

Having reacted with the metal in the thallium column, the solution flows (upward) into the counting cell. Since no liquid flow beta counter is commercially available which combines both high sensitivity with small volume and physical ruggedness, it was necessary to construct one for the purpose. The counting cell designed for this oxygen monitor consists essentially of two thin Teflon membranes --about 3 millimeters apart--between which the solution flows. Thin-window "pancake" Geiger-Mueller counters are pressed against the Teflon membranes and count the beta particles coming from the solution. The volume of the counting cell is about 5.3 ml., the two surface areas total 35 $cm^2$, and the Teflon membranes are 2 mils thick. Under these conditions, the efficiency of the counting cell for $Tl^{204}$ is about 2.7 percent. Figures 4-7 show construction details of the counting cell.

The Geiger-Mueller counters used are Anton No. 1008T. The Teflon part of the counting cell, No. 10 in Figures 4 and 6, is machined so that the two counters fit snugly in the hole and rest on the shoulder of the part. The 2 mil Teflon membrane fits between the mica windows of the counter and the shoulder of the Teflon part. It was found during early tests that, even though the two counters were pressed tightly against the shoulder and the membrane, the membrane stretched under the pressure of the water in the cell sufficiently to endanger the thin mica windows of the counters. Therefore, a piece of screen wire was placed between the membrane and the counter to eliminate the possibility of breaking the window. A thin stainless steel washer is then necessary between the membrane and the screen wire to distribute evenly the pressure from the compression backing plates, Part 11, through the edges of the screen wire. In Figure 8 the screen wire can be seen resting in place in the Teflon Part 10. Parts 11 and 12 of Figures 4, 6 and 7, are used to apply pressure by means of screws into Part 9, on the backs of the counters

to make a leak-tight seal between the membrane and the shoulder of Part 10. Figure 9 shows one of the counters in place in Part 10, preparatory to placing the whole in Part 9 and screwing on the pressure plate, Part 11. The thallium column is also ready to be inserted into its receiver in Part 10.

The original counting cell, as shown in the construction Figures 4-7, was designed to have the inlet from the thallium column at the bottom, and the outlet at the top. This arrangement proved unsatisfactory. It was shown by temporarily substituting transparent membranes for the Teflon membranes and passing a colored liquid through the cell, that many minutes were required to replace the original liquid. Direct streaming from bottom to top occurred. Rapid mixing was obtained when the outlet was changed to the side, at 90° from the inlet. Replacement of the original liquid with the opaque liquid was then seen to be almost instantaneous under the same flow rate as the above experiment.

Part 10 was therefore modified to have a third orifice drilled at right angles to the original two, as shown in Figures 8 and 9. This made possible the addition of a decontamination inlet at the top of the counting cell. If build-up of contamination occurs in the counting cell, with resultant increase in background of the instrument, it is unnecessary to dismantle the cell. It is possible to close off the thallium column by means of stopcocks, and pour a decontaminating solution through the cell.

4) Ion Exchange Column

When the dissolved oxygen analyzer is used in the field, it may not be desirable to allow the radioactive effluent to be returned to the environment. Therefore, provision has been made to pass effluent from the counting cell through an ion-exchange column where the thallium is retained. This column is a cylinder of copper, 1 inch in diameter by 6 inches long, and contains 25 grams each of Dowex-50 and Dowex-1A ion-exchange resins. The theoretical capacity of the resin

is several times the quantity of thallium which can be packed in the thallium column. Washing out--desorption--of adsorbed thallium from the ion-exchange column was measured by passing tap water through the column until $Tl^{204}$ was detected in the effluent. More than 20 liters of tap water were required before $Tl^{204}$ appeared. The "clean-up" column is therefore satisfactory for collecting the total charge of thallium in the thallium column, should it be necessary in field work.

The ion-exchange column can be by-passed, by manipulating the proper stopcocks, whenever it is possible to collect the radioactive effluent from the instrument and dispose of it in a different manner.

5) Electronics

Electronics are battery operated and transistorized. The circuit diagram, shown in Figure 10, is adapted from conventional circuitry[3,4]. High voltage for the Geiger-Mueller counters is obtained from a transistorized supply (Universal Transistor Product Corporation No. E 1200-3-50) which is further regulated in the instrument. Originally it was thought desirable to monitor the high voltage on the Geiger-Mueller counters by means of the panel meter. This caused too much power drain from the power supply (maximum current - 50 microamperes), that the convenience of being able to monitor the voltage on the panel meter did not seem worth the extra circuitry needed to accomplish it. The optimum high voltage is chosen and set in the laboratory and checked periodically thereafter with a high impedance voltmeter (100 megohms or more).

The count rate from the counters is displayed on a panel meter. Four decades of count rate are obtainable by means of a range switch. It has been found desirable at times to make use of a scaler, rather than the count rate circuit.

---

[3] M. C. Kopp, ORNL-TM-330, August 23, 1962, "A Transistorized Alpha Counter for an Alpha Gauge".

[4] R. P. Burr, Mil-Hdbk-215, June 15, 1960, "Circuit 3-6 High Input Impedence Preamplifier".

Therefore, provision is also made in the instrument to bring the signal from the counters to an external portable scaler.

Figure 11 is a front view of the complete analyzer with the sample bag in position. A small plastic funnel is also in position just to the right of the sample bag, which serves as an entrance port for decontaminating solutions.

Figure 12 is a rear view of the analyzer, showing again the sample bag, the funnel for decontaminating solution, and also the barometer. This latter is used for measuring atmospheric pressure when calibrating the instrument.

Figure 13 is a view of the inside of the dissolved oxygen analyzer showing the two sample inlets and the thallium cell with the counting cell directly above. The outlet from the counting cell is at its center left. The effluent from the cell can be led through the ion-exchange column seen in the center of the container, or led directly to the stopcock and outside, visible just to the left of the column. All the electronics are at the left of the analyzer and the batteries are at the bottom of the Figure.

## IV. Operation and Characteristics of the Dissolved Oxygen Monitor

### 1) Preparation of Radioactive Thallium Metal

It is not possible to purchase $Tl^{204}$ in metallic form. The desired quantity of thallium, as the nitrate, is dissolved in about 200 ml of water and enough $Tl^{204}$ is added to give the desired specific activity. (The thallium column will hold about 5 grams of metal, sufficient for more than 20 liters of air saturated water. Two millicuries of $Tl^{204}$ per gram of metal gives about 50,000 counts per minute with air saturated water--8 PPM of oxygen). Thallium is deposited from a solution containing 10 grams per liter of thallium and 10 grams per liter of bacto peptone. Two platinum electrodes are inserted and the metal is reduced electrolytically by applying about 7 volts DC. Considerable evolution of $H_2$ and $O_2$

results from use of this rather high potential. The peptone is necessary to prevent deposition of thallic oxide at the anode. After reduction of thallium is complete the cathode and any loosened metallic thallium are transferred to a small beaker of acetone. The beaker is cooled in dry-ice-acetone slush after which the thallium metal, having become hard at the low temperature, is scraped off in large pieces. The thallium is then carefully packed into the thallium column, care being taken to avoid forcing the soft metal into a non-porous mass. In the earlier part of this work zinc strips were used to precipitate the thallium; however, it was learned that the metallic deposits contained both zinc and thallium which is unsatisfactory for our purposes.

2) Calibration of the Dissolved Oxygen Analyzer

Calibration of the instrument should be required only after each recharge of the thallium column. Since the observed count rate is a function only of the dissolved oxygen content of the influent sample solution and the specific activity of the $Tl^{204}$, so long as the counter characteristics remain constant, there should be no variation in count rate for a given oxygen concentration.

After considering several possible procedures for calibrating the instrument, that procedure which appears to have the fewest disadvantages was adopted. It is usable both in the laboratory as well as the field. In brief, the calibration is based on the known solubility of oxygen in water at given temperatures and pressures.

A bottle is partially filled with water and shaken vigorously several times over a period of half an hour, the bottle being opened to the air several times during the equilibration. Atmospheric pressure given by the barometer on the back of the dissolved oxygen analyzer is noted and the temperature of the water is measured. Figure 14 gives the family of curves relating solubility of oxygen in water at various temperatures and pressures. The sample of water is then passed

through the instrument until a steady counting rate is observed. The count rate for the given oxygen concentration is thereby obtained, but, since the count is directly proportional to oxygen concentration -- that is, the count rate – oxygen concentration curve is linear -- the instrument is calibrated for all oxygen concentrations.

This procedure has been checked by making dissolved oxygen determinations by the Winkler method and has been found to be quite satisfactory. Figures 15 and 16 are experimental curves of count rate as a function of dissolved oxygen concentration. These were obtained by mixing various proportions of nitrogen and oxygen and bubbling the mixture through a sample of distilled water for several hours.

3) Flow-Rate Dependency

Since the instrument's principle is based on a chemical reaction, it is possible to flow a sample through the thallium column faster than the kinetics of the reaction will permit complete reduction of the oxygen. That is, it may be observed that count rate is a function of flow rate of a given sample through the instrument. This may be especially true when the quantity of thallium in the column becomes depleted, or if the particles of thallium in the column are so loosely packed that many voids exist.

To check flow rate dependency of the instrument, a series of experiments were conducted. A large volume of water was equilibrated with air and then allowed to flow through the instrument at known flow rates. Table I shows the results. These data were taken with the thallium column loaded with 5 grams of thallium. As the quantity of metal is reduced, the apparent flow-rate dependency of the instrument will become more acute.

Table I

Response of Instrument to Sample Flow Rate

| Flow Rate in ml/min | Count Rate cpm |
|---|---|
| 1.5 | 55,000 |
| 1.9 | 54,800 |
| 4.4 | 55,700 |
| 9.0 | 51,500 |

4) Temperature Dependency

Again, since the principle of the instrument is based on a chemical reaction, there may be some effect of temperature on the observed count rate. This will be closely associated with flow rate dependency discussed immediately above.

An experiment was carried out to measure the effect of temperature on the reaction. The instrument was temperature equilibrated in a room at 6°C. Samples of water equilibrated with the instrument were then passed through it at known flow rates. (Count rates observed in the cold room are greater than those at room temperatures because of the differences in solubility of oxygen in water at the two temperatures.) Results are shown in Table II.

Table II

Analyzer Response Dependency on Flow Rate at 6°C

| Flow Rate in ml/min | Count Rate cpm |
|---|---|
| 1.0 | 63,000 |
| 1.9 | 63,600 |
| 3.0 | 59,700 |
| 3.8 | 58,700 |

This experiment suggests that there is no pronounced temperature effect in the range of 6°C to 25°C.

It should be pointed out that the reaction rate is a function of the area of

the thallium exposed to the water. Thus, each column will have a flow-rate effect and temperature-effect which is characteristic of the thallium particle size and amount of thallium present. Thus, flow-rate data at different temperatures will be different for each column. A single low temperature measurement was made to determine that there was no appreciable temperature effect in this temperature region.

5) Interferences

Most salts -- ionized, unionized and soluble organic compounds -- have no action on thallium. Strong oxidizing agents will oxidize thallium as will low pH. The separate responses for $0_2$ in distilled water and sea water shown in Figures 15 and 16 suggest that salts in the sea water do interfere. The thallium used in the column for these experiments had previously been precipitated by insertion of zinc strips and originally contained co-precipitated zinc. Subsequent precipitations, done with a platinum electrode and an electric current, probably retained some zinc. The zinc, being more reactive than the thallium, probably removed a substantial amount of dissolved oxygen before it reacted with the thallium. The chloride ion present in sea water would enhance this side reaction and produce the low sea water readings. This type of reaction was clearly shown for thallium plated on copper turnings in our early work.[1] A careful study was made of radio-release from a zinc-free thallium-204 column with distilled and sea waters. Released thallium was assayed radiometrically and chemically. Dissolved oxygen was determined by the Winkler technique. Results are shown in Table III.

Table III

Air Saturated Sea Water and Distilled Water Radio-Release

| Type of $H_2O$ | $\mu$ eq Tl/ml | $\mu$ eq $0_2$/ml | Ratio $Tl/0_2$ | CPM/PPM $0_2$ |
|---|---|---|---|---|
| Distilled | 1.03 | 0.24 | 4.30 | 6900 |
| Sea | 0.862 | 0.195 | 4.25 | 6750 |

The count rate responses found for sea water and distilled water agree to within 2.2% which is probably as good as the experimental accuracy for this work.

Samples having pH values less than 5 cannot be used. However, raising the pH by addition of base, if it does not lead to absorption of oxygen from the air during the addition, is a remedy. Solutions buffered to pH values above 5 are satisfactory. Any modification of the oxygen concentration must be considered.

Nitrate ion does not interfere if its concentration is less than 100 milligrams per liter. Above this concentration, nitrate ion slowly reacts with the thallium at pH values above 5.

Dichromate ion does not oxidize thallium at pH 8. Whether at lower pH values it can do so has not been studied. It would be an unusual circumstance, however, in which there were interfering amounts of dichromate in the water.

6) Application to Sewage Plant Effluent Solutions

An important use of a dissolved oxygen analyzer is in monitoring oxygen in various fermentation processes. Use of this radio release method to assay oxygen in sewage processing vats is impractical unless precautions are taken to prevent the column from being plugged by the process sludge. One important measurement, however, is the oxygen concentration in the sewage plant effluents discharged into rivers and streams. Too low an oxygen content in this effluent is often a cause of fish kills. The dissolved oxygen analyzer was taken to the largest sewage processing plant in Durham, North Carolina and used to measure oxygen in the effluent solution being discharged into an aqueduct carrying it to a river.

Dissolved oxygen determinations were made by the radio release method, by a Yellow Springs Scientific Instruments polarographic analyzer, and by the Winkler method of chemical analysis. Results are compared in Table IV.