The Determination of Dissolved Oxygen by the Use of Its Stoichiometric Reaction with Metallic Lead

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The study of the quantitative determination of minute amounts of dissolved oxygen is receiving particular attention, with special regard being paid to the control of the oxygen content of feeding water to a high-pressure boiler plant, or to the biochemical processes.

Among the many techniques proposed for the estimation of oxygen dissolved in water,[1] the method based on the oxidation and dissolution of metal is thought to be most promising.

The oxidation of metallic thallium to a thallous ion and subsequent determination by means of the electric conductivity,[2] the radioactive ^{204}Tl tracer technique,[3,4] or by polarography[4] have been investigated recently; also a several p. p. m. concentration of oxygen has been measured by the oxidation of zinc amalgam[5] or copper metal[6,7].

The authors, in the course of a study of the reaction of metal and dissolved oxygen, noticed a stoichiometry in lead-aqueous oxygen system.

The resultant of the reaction was lead hydroxide, which can be dissolved with an acetic acid and sodium acetate solution, whereas lead metal is not bitten by the acetate mixture. The reaction is conjectured to be:

$$Pb + 1/2O_2 + H_2O \rightarrow Pb(OH)_2$$

$$Pb(OH)_2 + 2CH_3COOH \rightarrow Pb(CH_3COO)_2 + 2H_2O$$

or

$$Pb + 1/2O_2 + 2CH_3COOH \rightarrow Pb(CH_3COO)_2 + H_2O$$

The eluted plumbous ion was determined directly by a. c. polarography. Useful information was obtained thus for designing a method of determining the oxygen dissolved in water.

Experimental, Results and Discussion

The sample solution was prepared by boiling pure water in an atmosphere of nitrogen, and the dissolved oxygen content was calibrated by the amperometric titration with two polarized electrodes, as reported by Potter and White.[8] The standardized sample solution was fed to the reaction column (diam. 1.2 cm., height 7.0 cm.), which had been filled with metallic lead grain (diam. 2—3 mm.), together with a 50% acetic acid solution, saturated with sodium acetate. The schematic diagram of the experimental system is shown in Fig. 1.

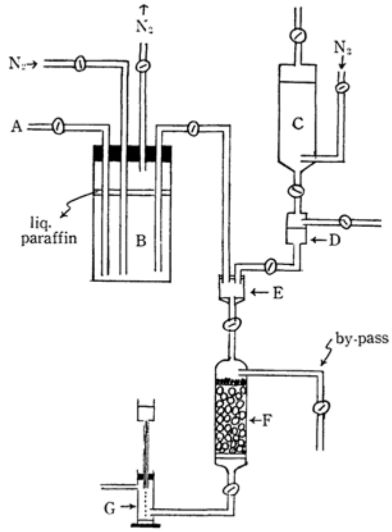

Fig. 1. Schematic diagram.

A: To the amperometric titration
B: Sample preparation and storage tank
C: Deaerated acetate buffer and storage tank
D: Constant head device
E: Mixing cell
F: Lead column
G: Polarograph cell for continuous measurement

The volume ratio of the acetic acid - sodium acetate mixture to the sample solution was 1.43 to 0.01. The eluted solution was received directly in

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a electrolytic cell, the quantity of lead was determined by measuring the wave height of the a. c. polarogram.

The results of this experiment are shown in Table I.

TABLE I. THE STOICHIOMETRY OF $Pb+1/2O_2+2CH_3COOH \rightarrow Pb(CH_3COO)_2+H_2O$ REACTION

Oxygen content in sample sol. (p.p.m.)	Quantities of lead dissolved per ml. calcd. (μg.)	Dissolved quantities of lead. obsd. (μg.)	Obsd./Calcd.
7.50	97.5	96.0	0.98
4.86	63.2	65.7	1.04
3.14	40.8	37.5	0.92
2.80	36.4	38.0	1.04
1.51	19.6	22.5	1.15
0.34	4.4	7.2	1.64

The stoichiometry of the $Pb+1/2O_2+2CH_3COOH \rightarrow Pb(CH_3COO)_2+H_2O$ reaction above the p.p.m. region could be confirmed because the ratio of the observed to the calculated quantity of dissolved lead was approximately one.

Accordingly, the linearity of the aqueous oxygen content vs. the dissolved lead is perfect in the 1—10 p.p.m. range.

The completeness of the reaction of a metallic lead and aqueous oxygen was confirmed by the fact that no oxygen reduction wave was detected in the polarogram. Though a marked departure from the stoichiometrical linearity was observed for the extremely low oxygen content solution, this seems to result from the leakage of air into the sample and the acetate buffer solution, through polyvinyl tubings or through the interstice between polyvinyl and glass tubings in the course of the experiments. The advantages of the lead column method over the other methods (especially the thallium column method) will be outlined below:

(1) A lead column can be used effectively for a weak acidic sample, whereas the thallium method results in a serious positive error due to the dissolution of metallic thallium by a sample solution.

(2) A lead column can be readily prepared by filling the commercially-available lead grain in a glass tubing.

(3) The lead is more immune to oxidation by air than is the thallium.

(4) The dissolved quantities of lead can be determined by the use of the radioactivity, as ^{210}Pb is readily available.

(5) The lead-column method is readily applicable to the continuous measurement of the aqueous oxygen content.