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Practical Coulometric Detectors of Dissolved Oxygen

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1 INTRODUCTION

The measurement of dissolved oxygen (DO) is inevitable for monitoring the water quality of rivers, lakes and a greater part of water treatment facilities. Most of commercially available DO analyzers employ the methods of amperometry or potentiometry, such as a galvanic cell. However, the conventional electrochemical DO analysers still have some problems since the careful maintenance and calibrations within short period are needed to keep their reliability. Some laboratories, in practice, have begun to adopt redox potential measurements to control waste water treatment facilities in stead of the control by DO measurements.¹⁾ The DO analysers have been expected to be improved in these points.

Coulometric DO measurements give us novel means of solving the problems, since no calibration is needed, and high accurate and reliable monitoring can be expected. The coulometric technique can play an important role in a DO measuring field. In this note, we intend to demonstrate the two type of coulometric detectors; one is a rapid coulometric detector, the other is a flow cell type for continuous DO monitoring.

2 EXPERIMENTAL

The basic configuration of the coulometric detector was as described earlier.^{2, 3)} In the DO detector, high purity nitrogen gas was introduced on the working electrode to isolate from the external atmosphere. The carbon fiber felt 38mm diameter, 3mm thickness) of the working electrode

Fig.1 DO detector configuration and block diagram of the experimental system.

- A : working electrode, (carbon felt, 38mm diameter, 3mm thickness),
- B : cation-exchange membrane (Asahi Glass Cellemion, C.M.V.),
- C : counter electrode, (carbon felt, 38mm diameter, 3mm thickness),
- D : sample,
- E : nitrogen gas,
- F : cell holder
- G : detector,
- H : potentiostat (Hokuto Denko HA502),
- I : coulometer (Hokuto Denko HF203D),
- J : recorder.

were coated with approximate 10mg of platinum by using a method of non-electrolytic plating method. The working and counter electrodes were impregnated in 0.5M sodium acetate-acetic acid solution (pH4.5) containing 0.3M potassium hexaferrocyanide, and 0.5V was applied between these two electrodes. In these conditions, the electrode reaction proceeds readily.²⁾ The cross section of this detector and the experimental system are shown in Fig.1.

Pure water was used as the sample for the DO determination. The concentrations of DO were adjusted by introducing high purity nitrogen gas and determined by Indigo Carmine method.⁴⁾ The sample solutions were dropped into the center of working electrodes with a 50 μ l or a 100 μ l Eppendorf pipet after the residual current of detectors reached constant steady-state values.

In the next step, for the demonstration of continuous DO monitoring, a flow cell was also fabricated by using an ion-exchange membrane tube. The configuration of the flow cell is shown in Fig.2, and a piece of Nafion 117 tubing was

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Fig.2 The structure of a flow coulometric DO detectors.

- A, A': carbon plates,
 B: working electrode (carbon felt, 100mm length, 10mm width, 3mm thickness),
 C: cation exchange membrane,
 D: counter electrode (carbon felt),
 E: sample solution inlet,
 F: sample solution outlet,
 G: nafion 117 tubing,
 H, H': plastic plates,
 I, I': silicon rubber gasket.

Fig.3(1) The current vs. time curves obtained for the determination of dissolved oxygen in pure water.

(A): 50 μl sample soln. (B): 100 μl sample soln.
 D.O.: 1.100 mg l^{-1} (Indigo Carmine Method)
 W.E.: -0.5V vs. C.E.
 Electrolyte: 0.5M AcONa-AcOH soln. containing
 0.3M potassium hexaferrocyanide, pH4.5

27°C

Fig.3(2) The current vs. time curves obtained for the determination of dissolved oxygen in pure water.

(A) 50 μl sample soln. (B) 100 μl sample soln.
 D.O.: 0.030 mg l^{-1} (Indigo Carmine Method)
 W.E.: -0.5V vs. C.E.
 Electrolyte: 0.5M AcONa-AcOH soln. containing
 0.3M potassium hexaferrocyanide, pH4.5
 27°C

employed for sampling the solutions. The coulometer was removed from the experimental system in this case.

3 RESULT AND DISCUSSION

In the cell shown in Fig.1, current vs. time curves obtained for the determinations of 1.10 mg l^{-1} , and 0.03 mg l^{-1} of DO are shown in Fig.3.

Fig.4 The relationship of DO determinations between the coulometry and the Indigo Carmine Method.

Sample : pure water,
 Detector

Electrolyte : 0.5M AcONa-AcOH soln. containing
 0.3M potassium hexaferrocyanide,
 pH4.5,

W. E. : -0.5V vs. C. E.,
 Sample volume : 100 μl ,
 27°C.

Fig.5 The current vs. time curve obtained by the flow coulometric DO detector

Sample : pure water,

Detector

Electrolyte : 0.5MAcONa-AcOH soln. containing 0.3M potassium hexaferrocyanide, pH4.5,

W. E. : $-0.5V$ vs. C. E.,

Sample flow rate: 5 ml min^{-1} ,
 25°C .

Considering to the current-time curves for the 0.05 and 0.03 mg l^{-1} determinations, the lower limit of this detector was found to be approximate 0.05 mg l^{-1} (50ppb). The determination of DO lower than 0.05 mg l^{-1} was disturbed by the fluctuation of back-ground current due to the change of double layer capacitance when a sample solution was dropped to the working electrode surface. The electrolysis time was dependent on the concentration of DO, and within 50 seconds at most. Figure 4 shows the comparison between the coulometry and the Indigo Carmine method for the DO determination. This figure indicates that the results obtained by the coulometric detector are in fairly good agreement with those obtained by Indigo Carmine method.

Fig. 6 The relationship of DO determinations between the flow coulometric detector and a commercial galvanic cell.

Sample : effluent of a waste water treatment facility,
 flow rate : 5 ml min^{-1} ,
 DO meter : galvanic cell type, DKK-DO-31.

It is ordinary for automatic DO analyzers to be operated continuously, and can be anticipated to improve coulometric determinations of DO by introducing the flow cell technique using a ion-exchange membrane tube. An typical current vs. time curve obtained by the flow coulometric cell is shown in Figure 5. The increasing and decreasing of current was proportional to the DO concentration of samples. The electrolytic current subtracted by back-ground level is related to the DO concentration as follows;

$$I = \frac{2FCL}{16 \times 60 \times 10^3} = 0.20 CL,$$

Where I , C and L are the current (mA), DO concentration (mg l^{-1}) and the sample flow rate (ml min^{-1}), respectively, and F is Faraday constant. The above relationship was applicable to the region of below 7 ml min^{-1} of the flow rate. Fig.6 shows a relationship of DO determinations between the flow coulometric detector and a commercial galvanic cell. As shown in Fig.5 and Fig.6, the performance of flow coulometric detector become more stable and reliable by introducing an ion exchange membrane tubes.

This flow cell technique is expected to be available not only for DO determination but for components in liquid and gaseous samples.

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