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New Coulometric Detectors for Dissolved Organic Material Monitoring

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1 INTRODUCTION

Measurements of water pollution level related to organic contaminants are especially important in monitor stations of lakes and rivers as well as in various water treatment facilities. However, it is not easy to observe the pollution level, such as COD, BOD, TOC, DOC etc., automatically, because the automatic monitors for these pollution level measurements are too complicated in their operation and maintenance compared with conventional DO, pH and SS measurements.

Recently, the measurement of ultraviolet absorption at 250 nm has been used to estimate the COD or DOC levels due to its simple structure and operation, and has taken into the Japan Industrial Standard (JIS) method for the analyses of waste water. Dissolved components of organic materials mainly consist of humified materials and lower hydrocarbons such as carboxylic acids, and relatively favorable correlation is observed between their concentrations and the ultraviolet absorption.^{1,2)} However, this correlation is fluctuated by seasonal changes of climate and even by the daily variation of weather.

Coulometric determinations seem to be useful in solving these problems of water pollution monitoring, since the oxidation of dissolved components is similar to the basic reaction for COD or TOC determinations and coulometry can utilize these oxidizing reactions. In this note, we would like to demonstrate the availability of rapid coulometric estimation of water pollution level by determining dissolved organic materials.

Fig.1 Absorption spectra of sample solutions.

2 EXPERIMENTAL

A leach solution from a landfill ground for wastes was employed as the sample. The organic components in the solution are rich in humus type materials, and its COD and BOD were 464 mg l^{-1} and 285 mg l^{-1} respectively, which were measured by the JIS standard method. Another sample was prepared by ozone treatment of the leach solution. Ozone was introduced to the leach solution in the scrubbing bottle at the rate of approximate 1 g ozone per 1 l solution for 40 minutes at 20°C . Ozone decomposes a large part of dissolved organic substances and decreases the COD value of the solution. COD and BOD of the ozone treated solution were 139 mg l^{-1} and 110 mg l^{-1} respectively. Figure 1 shows the absorption spectra of the sample solutions before and after the ozone treatment.

Electrolytic cells for coulometric detectors are shown in Fig.2. The basic configuration of detectors are the same as those described in our previous studies,^{3,4)} except electrode materials, electrolytes and heating devices. In Fig.2 (1), the working electrode was a round porous carbon felt (Nippon Carbon, GF-20 felt, 38 mm diameter, 3 mm thickness) pregnant with vanadium (V) sulfate-sulfuric acid solution, and the same carbon felt with vanadium (II and III) sulfates-sulfuric acid solution was used as the counter electrode. These

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Fig. 2 Structures of organic materials detectors.

- A: working electrodes, B: ion-exchange membranes,
 B': glass fiber mat, C: counter electrodes,
 D: sample drops, E: nitrogen gas,
 F: cell holders. G: hot plates.

two electrodes were separated by ion exchange membrane (Nafion 117). A hot plate was employed as the heating device to keep the cell 60~70 °C. In case of Fig. 2 (2), lead dioxide and lead metal were used as the working and counter electrodes, respectively, which were separated by a sheet of glass fiber mat. The working electrode was prepared by electrochemical oxidation of lead monoxide powder which was filled up in a lead felt mat (40 mm diameter, 5 mm thickness, 0.2 mm fibril's diameter) in approximate 1~2 mol dm⁻³ sulfuric acid, and lead monoxide was also electrochemically reduced in approximate 1~2 mol dm⁻³ sulfuric acid on the counter electrode side. In the first stage of this formation process, current was maintained to be constant value (1 mA) for approximate two days, and succeedingly, 2.3 V was applied to the electrode in the second stage for approximate three days. This detector was also equipped with a heating plate to keep the cell at 60~70 °C.

Concerning quantitative characteristics, two types of detectors were checked by formic acid solution, and it was conformed that quantitative determinations with two electron oxidation would be carried out on both cells. The applied voltages of these two detectors were +1.5 V for the vanadium cell and +2.3 V for the lead dioxide cell, respectively. 10 µl of sample solutions were dropped into the center of working electrodes with Eppendorf pipets after the residual current of detectors had reached constant steady-state values.

In order to perform the controlled potential coulometric determinations, a potentiostat (Hokuto Denko, HA502) and a digital coulometer (Hokuto Denko, HF203D) were used and a recorder was employed to record the current vs time curve.

3 RESULTS AND DISCUSSION

Table 1 shows the result of determinations of two sample solutions using the vanadium (V) detector and lead dioxide detector, and a typical current-time curve obtained by the lead dioxide cell is shown in Fig. 3. The performance in the determination time and the accuracy was similar to our previous studies of the rapid coulometry.^{3,4)}

The original sample was dark brown solution and had relatively high COD value after the ozone treatment. The survived COD components seemed to consist of oxidation durable materials, however, some organic products formed by ozone oxidation could be changed into bacteria degradative materials which would be involved in BOD components. Therefore, the ratio of BOD/COD was increased after the ozone treatment.⁵⁾ The oxidation durable organic materials should be difficult to detect sufficiently by the vanadium (V) and the lead dioxide detectors.

The COD values of dissolved organic material (DOM) of the original sample solution were 180mg l⁻¹ for the vanadium (V) cell and 307mg l⁻¹ for the lead dioxide cell. The latter value seemed to correspond to the subtracted COD values on subtracting the COD value (KMnO₄) after ozone treatment from that of the original sample solution. Therefore, the lead dioxide cell could detect the ozone decomposable COD components, in contrast with the vanadium (V) detector which had less detective characteristics for such COD components. This result indicates that the lead dioxide detector is available to a controlling device of waste water ozone treatment systems. On the other hand, the vanadium (V) cell can be considered that the vanadium(V) cell is useful for determinations of relatively easy-oxidizing substances.

The reactions for COD or DOC measurements usually need high temperature, such as 70 °C or more high degree, to complete oxidation of organic materials. Coulometric detectors for DOC determinations also need high temperature to perform desirable operational time for analyses. However, since the cross-mixing rate of electroactive materials through the membrane separator extremely increases in such higher temperature region, the background current level raises and becomes unstable, which causes the decrease of the lower limit of DOM detection. The adoption of the electrode reactions of DOM without using any soluble redox mediators, such as vanadium (V/VI) and iodine (O/I), can solve the problem of cross-mixing, as well as the employment of insoluble electroactive materials in the working and counter electrodes. The lead dioxide detector is one of the devices to eliminate cross-mixing problem.

Table 1. Various dissolved organic material (DOM) values measured by titration method using KMnO_4 and vanadium (V) and lead dioxide coulometric detectors.

Sample	Titration using KMnO_4	Vanadium (V) detector				Lead dioxide detector			
	COD (mg-O l^{-1})	charge ^a (mC)	DOM (mg-O l^{-1})	RSD (%)	DT ^a (sec)	charge ^a (mC)	DOM (mg-O l^{-1})	RSD (%)	DT (sec)
Original	464	21.7	180	1.5	15	37.0	307	1.8	12
Ozone- treated	139	0.6	5	2.5	11	2.9	21.7	2.4	10

a : mean value of 5 data

COD : COD values

DOM : dissolved organic material value

$$\text{DOM (mg-Oxygen l}^{-1}\text{)} = \frac{\text{Charge(mC)}}{\text{Faraday Const.}} \cdot \frac{10^6 \mu\text{l l}^{-1}}{10 \mu\text{l}} \cdot 1 \text{ gram equivalent of oxygen}$$

DT : determination time

RSD : relative standard deviation

Fig.3 The current transient curve obtained for the determination of dissolved organic materials using the lead dioxide detector.

Another coulometric approach for COD measurements was proposed by K.I. Pamplin *et. al.*, using Cr (VI) ion as a redox mediator.⁶⁾ The COD values obtained by this coulometry considerably agreed with those of EPA method. However, this coulometric determination has the same problem as the vanadium(V) detector with a soluble redox mediator which permeates to the counter electrode and raises the background current. And generally, it takes much longer determination time for the DOM coulometry with redox mediators than that of the lead dioxide electrode method.

The rapid coulometric systems are easy to assemble into automatic DOM analysers, and specific information on dissolved organic materials can be obtained from each type of coulometric detectors. The coulometric DOM cell using lead dioxide detector would contribute for many kinds of water treatments as a novel monitoring method.

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