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## Lead-Selective Membrane Electrode Using Methylene Bis(diisobutyldithiocarbamate) Neutral Carrier

Satsuo Kamata\* and Kazuhiro Onoyama

Faculty of Engineering, Kagoshima University, Korimoto, Kagoshima 890, Japan

Poly(vinyl chloride) membrane and membrane-coated carbon rod electrodes for lead(II) ion detection were developed by using the methylene and tetramethylene bis(diisobutyldithiocarbamate) neutral carriers and *o*-nitrophenyl octyl ether as a plasticizing solvent mediator. The membrane electrode based on methylene bis(diisobutyldithiocarbamate) exhibited good properties with a Nernstian slope of 28 mV/decade and linearity range of  $10^{-2}$  to  $10^{-6}$  M for the lead(II) ion. This membrane rejects alkali-metal ions by a factor of at least  $10^2$  and alkali-earth-metal ions by  $10^5$ , although the copper(II) ion is not rejected.

The electrochemical properties and preparation of the lead(II) ion selective membrane electrodes have been studied by using active materials, one of which is the solid-state membranes made by sulfide, oxide, selenide, and other salts of lead together with silver sulfide (1-13) and the other is a liquid ion-exchange membrane (14-17). Recently, much interest has been paid to the ionophore ligands as sensing materials for neutral carrier type ion-selective electrodes due to the unique properties of the compounds. The ionophores with oxygen donor atoms have been usually studied for alkali- and alkali-earth-metal ion selective electrodes, and many selective ligands have been found for these metal ions (18-23). The lead ion selective electrodes were examined by using ionophores such as oxa- and dioxadithiocarbamides for PbX<sup>+</sup> ion determination (24) and dibenzo-18-crown-6 and its derivatives for Pb<sup>2+</sup> ion determination (25-27), in which each ligand has oxygen donor atoms. It is well-known that the sulfur donor atom coordinates with transition-metal ions to form metal complexes. Several organosulfur compounds have been examined for copper(II) ion selective electrodes and have been shown to be useful copper(II) sensor materials (28-32). It is therefore expected that the sensitive ionophore ligands with sulfur donor atoms would also develop the lead ion-sensing materials, because it is possible to modify the ligand structure to improve ion selectivity.

In this paper, we report on a sensing system involving the lipophilic ionophores of methylene bis(diisobutyldithiocarbamate) (MBDiBDTC) and tetramethylene bis(diisobutyldithiocarbamate) (TMBDiBDTC) with *o*-nitrophenyl octyl ether (NPOE) as plasticizing solvent mediator by using two types of electrodes: conventional membrane electrodes and membrane-coated carbon rod electrodes. These new ionophores, each having different C-shaped cavities with four donor sulfur atoms, were expected to form selective complexes with transition-metal ions and to give an improved selectivity for the lead ion.

### EXPERIMENTAL SECTION

**Reagents and Chemicals.** Poly(vinyl chloride) (PVC) and NPOE were obtained from Fluka (Buchs, Switzerland). Potassium tetrakis(*p*-chlorophenyl)borate (KTCBPB) as an anion excluder was obtained from Dojin Kagaku (Kumamoto, Japan). Carbon rods were obtained from Nippon Carbon Co. (Yokohama, Japan). All solutions were prepared from analytical reagent grade salts with distilled, deionized water. All other materials and chemicals were of the best available laboratory reagent grade.

**Preparation of MBDiBDTC and TMBDiBDTC.** Diisobutylamine (0.14 mol) and 2-propanol (25 mL) were dissolved in water (300 mL) containing sodium hydroxide (0.14 mol). This mixture was stirred at room temperature, while carbon disulfide (0.14 mol) was slowly added to the solution and allowed to react for 2 h. The precipitate of sodium *N,N*-diisobutyldithiocarbamate was filtered and crystallized from 2-propanol, yield 64%, mp 36-37 °C. The recrystallized sodium *N,N'*-diisobutyldithiocarbamate (0.05 mol) was dissolved in ethanol (300 mL), and methylene dibromide (0.025 mol) was added slowly to the solution with refluxing and stirring for 7 h. The final compound, MBDiBDTC, was obtained as white crystals and recrystallized from ethanol, yield 5.1 g, 60%, mp 69-70 °C. Anal. Calcd (found): H, 9.06 (9.05); C, 53.98 (53.96); N, 6.63 (6.65). IR (KBr), cm<sup>-1</sup>: 740 ( $\nu_{C-S}$ ). NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 0.93 (d, 24 H), 2.33 (m, 4 H), 3.65 (d, 8 H), 5.40 (s, 2 H). TMBDiBDTC was synthesized by reacting sodium *N,N'*-diisobutyldithiocarbamate (0.04 mol)

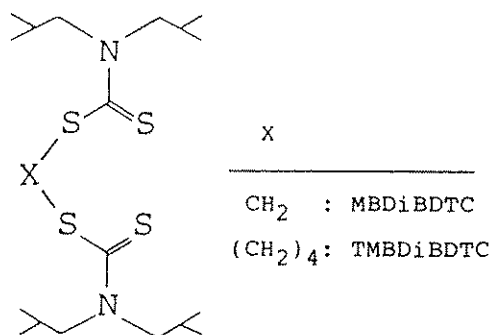


Figure 1. Sensor materials for the Pb(II) ion.

Table I. Membrane Composition of Pb(II)-Selective Membrane Electrodes<sup>a</sup>

component	membrane electrode		membrane-coated carbon rod electrode	
	1	2	3	4
ionophore	MBDiBDTC	TMBDiBDTC	MBDiBDTC	TMBDiBDTC
NPOE	11.2	12.4	12.7	11.0
KTCPB	49.6	49.4	52.9	53.0
PVC	2.0	1.2	2.0	2.1
	37.2	37.0	32.4	33.9

<sup>a</sup> Values are mass ratio in percent.

with tetramethylene dibromide (0.02 mol) in ethanol for 5 h, yield 6.4 g, 56%, mp 80–81 °C. Anal. Calcd (found): H, 9.54 (9.62); C, 56.84 (56.79); N, 6.03 (5.99). IR (KBr), cm<sup>-1</sup>: 725 ( $\nu_{\text{C-S}}$ ). NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 0.93 (d, 24 H), 1.83 (m, 4 H), 2.35 (m, 4 H), 3.33 (m, 4 H), 3.72 (d, 8 H).

#### Membrane Composition and Electrode Fabrication.

The method for preparing a PVC-immobilized ionophore membrane has been described previously (28). Ionophore, NPOE, KTCPB, and PVC were dissolved in 5 mL of tetrahydrofuran (THF). The THF solution was poured into a glass ring (35-mm diameter) on a glass plate and kept for 24 h at 30 °C to make a sensing membrane. The membrane electrode was made by fixing a disk (6-mm diameter) of the membrane to the PVC tubing. A membrane-coated carbon rod electrode was prepared as follows. The end of the carbon rod (2-mm diameter) was polished and then coated with a membrane by immersing 10 mm of it in the coating solution and drying it at room temperature several times. The electrodes were then soaked in a 10<sup>-3</sup> M solution of lead nitrate solution for 24 h before use. The optimized membrane compositions for two kinds of lead electrodes are summarized in Table I, respectively.

#### Electrode System and Electromotive Force (emf) Measurements.

All emf measurements were performed with the following cell assembly: Ag–AgCl/10<sup>-3</sup> M PbCl<sub>2</sub>/sensor membrane/sample solution/reference electrode for the membrane electrode and carbon rod/sensor membrane/sample solution/reference electrode for the membrane-coated carbon rod electrode. A Corning digital research pH meter (Model 112) was used for measuring the potential. The emf observations were made relative to a saturated calomel electrode (Iwaki Glass, Tokyo, Japan) in solutions stirred with a magnetic stirrer. The performance of the electrodes was examined by measuring the emfs of lead nitrate solutions prepared with a concentration range of 10<sup>-1</sup> to 10<sup>-8</sup> M by serial dilution. The activities of metal ions were based on activity coefficient ( $\gamma$ ) data calculated from the modified form of the Debye–Hückel equation:

$$\log \gamma = -0.511z^2[\mu^{1/2}/(1 + 1.5\mu^{1/2}) - 0.2\mu]$$

where  $\mu$  is the ionic strength and  $z$  is the valency. All the

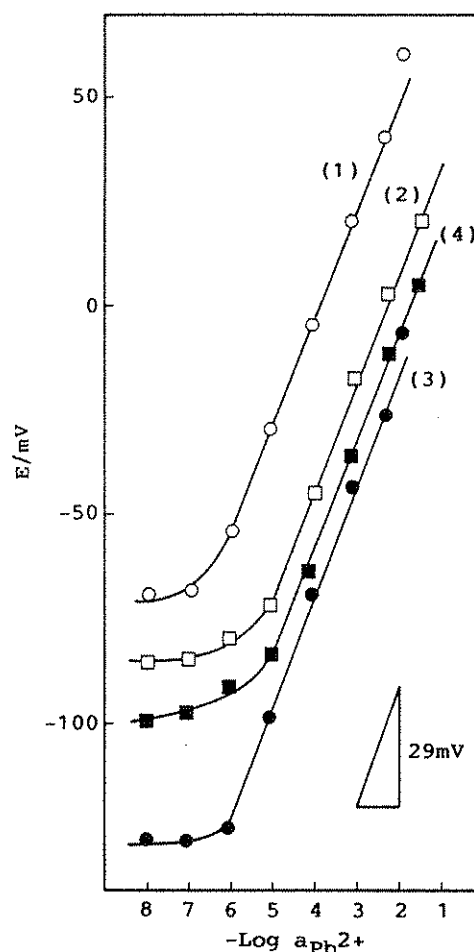


Figure 2. Electrode response for the Pb(II) ion in Pb(NO<sub>3</sub>)<sub>2</sub> solution. Composition of conventional membrane electrodes: (1) MBDiBDTC, (2) TMBDiBDTC. Composition of membrane-coated carbon rod electrodes: (3) MBDiBDTC, (4) TMBDiBDTC.

measurements were carried out at 25 ± 0.1 °C, using a Coolnit BCL-19 thermostat (Taiyo Kagaku Kogyo, Tokyo, Japan). All the metal nitrate solutions were freshly prepared by dilution from their stock standard solution of 0.1 M with distilled, deionized water. The concentrations of metal ion were compared with the standard metal solutions on an atomic absorption spectrophotometer (AAS) by using an AAS Model SAS-727 (Daini Seikosha, Nagoya, Japan).

## RESULTS AND DISCUSSION

The calibration graphs of lead-selective PVC membrane electrodes are shown in Figure 2, comparing them with those of the membrane-coated carbon rod electrodes. The membrane electrode with MBDiBDTC (1) showed a Nernstian slope of 28 mV/decade with a straight line between 10<sup>-2</sup> and 10<sup>-6</sup> M Pb(NO<sub>3</sub>)<sub>2</sub>. On the other hand, the membrane electrode with TMBDiBDTC (2) exhibited a linearity range of 10<sup>-1</sup> to 10<sup>-5</sup> M Pb(NO<sub>3</sub>)<sub>2</sub>, which was shifted to a higher concentration than that of the MBDiBDTC electrode. The same tendency for the linearity range was also observed in the calibration graphs of the membrane-coated carbon rod electrode, as demonstrated in (3) and (4) in Figure 2. The properties of two types of membrane electrodes, i.e., conventional PVC membrane electrodes and membrane-coated carbon rod electrodes, are summarized in Table II.

The pH response profiles for electrodes were examined by use of 10<sup>-3</sup> M Pb(NO<sub>3</sub>)<sub>2</sub> solution, adjusted with nitric acid (0.1 M) and sodium hydroxide (0.1 M) as acidic and alkaline media. Each electrode gave a useful pH range of 2.9–5.5. The MBDiBDTC membrane electrode can be used in a wide pH

Table II. Properties of Pb(II)-Selective Membrane Electrodes

property	membrane electrode		membrane-coated carbon rod electrode	
	1	2	3	4
ionophore	MBDiBDTC	TMBDiBDTC	MBDiBDTC	TMBDiBDTC
detection limit, M	$3.5 \times 10^{-7}$	$7.9 \times 10^{-6}$	$1.6 \times 10^{-7}$	$3.2 \times 10^{-6}$
slope, mV/decade	28	29	27	28
response time, s	16	8	11	6
pH range <sup>b</sup>	3.1-5.4	3.3-5.4	2.9-5.5	3.5-5.5

<sup>a</sup> 95% value of steady potential measured with rapid 10-fold increase in  $Pb^{2+}$  concentration, i.e., from  $10^{-3}$  to  $10^{-2}$  M. <sup>b</sup> Measured in  $10^{-3}$  M  $Pb(NO_3)_2$  solution.

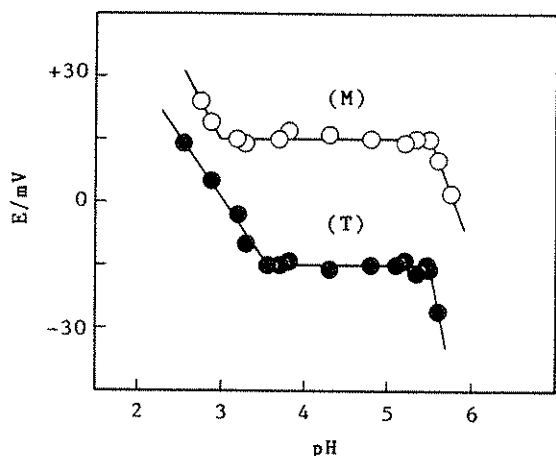


Figure 3. Effect of pH range on the Pb(II) ion, membrane-coated carbon rod electrodes based on ionophores of (M) MBDiBDTC and (T) TMBDiBDTC.

range. The influence of the pH response on each of the electrodes is shown in Figure 3.

At above pH 5.5, the potential decreased due to the formation of lead hydroxide in solution, while, at a lower pH, potential increased, indicating that the electrodes responded to hydrogen ion. The response time of the electrode was tested by measuring the time required to achieve a 95% steady potential for a  $10^{-2}$  M solution, when  $Pb(II)$  ion concentration was rapidly increased 10-fold from  $10^{-3}$  to  $10^{-2}$  M. The electrodes based on MBDiBDTC and TMBDiBDTC achieved a steady potential within 16 and 8 s for the membrane electrodes and 11 and 6 s for the membrane-coated carbon rod electrodes, respectively. The response times for the membrane-coated carbon rod electrodes are shorter than those for the membrane electrodes, due to the thin film (100  $\mu m$ ) that formed on the carbon rod surface. That the response time of TMBDiBDTC for the lead ion is a little faster than that of MBDiBDTC is probably related to the rate of complex formation. The selectivity coefficients ( $K_{Pb,B}^{pot}$ ) of each electrode for various cations were evaluated by the mixed-solution method (33, 34), with a fixed concentration of interferent, B, for which the concentration was  $10^{-1}$  M, except  $10^{-3}$  M for  $Zn^{2+}$  and  $Fe^{3+}$  and  $10^{-5}$  M for  $Cu^{2+}$ , in  $Pb(NO_3)_2$  solution of  $10^{-1}$  to  $10^{-8}$  M. The selectivity coefficient values for the electrodes are summarized in Figure 4.

Both electrodes based on MBDiBDTC and TMBDiBDTC were strongly interfered with by the copper(II) ion. This indicated that both ionophores with four sulfur atoms form complexes with copper(II) ion easily, regardless of the difference of distances between two dithiocarbamate groups, due to strong interaction of copper(II) with sulfur. Further, both electrodes were poisoned by silver(I) and mercury(II) ions.

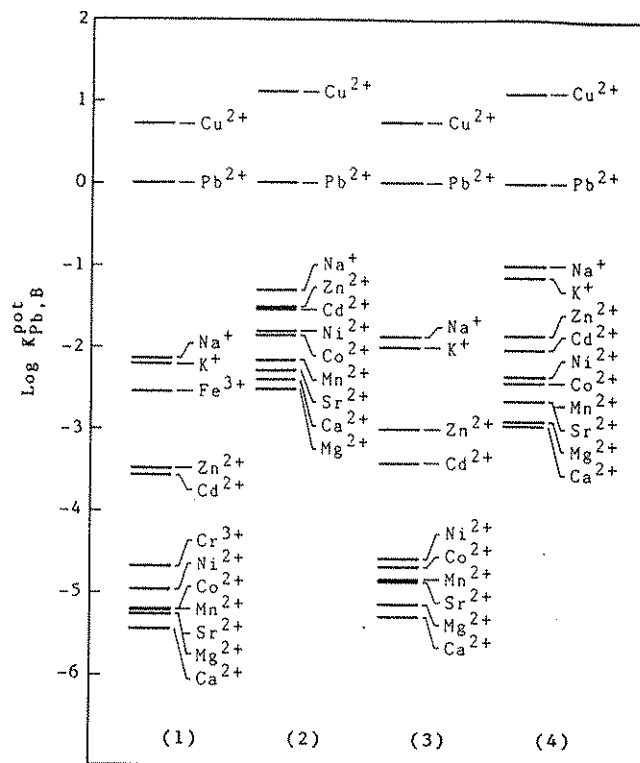


Figure 4. Selectivity coefficient ( $K_{Pb,B}^{pot}$ ) for the Pb(II) ion, incorporating different metal cations. The electrode construction is as follows: conventional membrane electrode (1) MBDiBDTC, (2) TMBDiBDTC; membrane-coated carbon rod electrode, (3) MBDiBDTC, (4) TMBDiBDTC.

The MBDiBDTC membrane electrode showed better selectivity factors for different metal cations than that of the TMBDiBDTC membrane electrode. This means that the coordination or uptake of lead ion by an ionophore is mainly related to the size of the C-shaped cavity of the ligand. The lead ion coordinates weakly with the donor sulfur atom compared with the case of the copper(II) ion. The MBDiBDTC membrane showed, therefore, good selectivity, having an ideal sized C-shaped cavity for the lead(II) ion. On the other hand, TMBDiBDTC has a long distance and free rotation between two dithiocarbamate groups linked by the four carbon chains of the ligand molecule and also has a large C-shaped cavity. Indeed, the  $Pb(II)$  ion in aqueous solution with  $ClO_4^-$  was extracted into 1,2-dichloroethane solution containing MBDiBDTC or TMBDiBDTC ionophores. Extractability was 10.8% and 1.2% for each ionophore, respectively. This means that the lead(II) ion was coordinated more strongly with the MBDiBDTC ionophore than with the TMBDiBDTC ionophore. Therefore the selectivities for the TMBDiBDTC membrane was not so good, because the  $Pb(II)$  ion is loosely coordinated with TMBDiBDTC and exchanged easily by different metal ions. No differences in the selectivity for different ions between the membrane electrode and the membrane-coated carbon rod electrode was observed. The membrane electrode based on MBDiBDTC responded to lead(II) ion and showed good sensitivity properties and selectivities in comparison to the membrane with the dibenzo-18-crown-6 ionophore (27). Except for the copper(II) ion, the selectivity of different cations for the membrane electrode with MBDiBDTC exhibited nearly the same tendency as the membrane based on the dioxadecarbamide compound (24), although the latter electrode responded to the monovalent lead ion,  $PbX^+$ , formed with the anion ( $X^-$ ).

It is considered that MBDiBDTC is a good sensor material for the lead ion due to the ideal size of the C-shaped cavity of the compound, which fits the lead(II) ion, and also due to

the lipophilicity of the ionophore.

### CONCLUSION

The sensitive and selective electrodes for the lead(II) ion based on MBDiBDTC and TMBDiBDTC were developed by using the conventional membrane electrode and membrane-coated carbon rod electrode. The MBDiBDTC membrane electrode exhibited good properties for a Nernstian slope of 28 mV/decade, linearity range, and selectivity factor of different metal ions, because of the ideal size of the C-shaped cavity fitting the lead(II) ion.

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## Microwave Acid Digestion and Preconcentration Neutron Activation Analysis of Biological and Diet Samples for Iodine

Raghunadha R. Rao and Amares Chatt\*

Trace Analysis Research Centre, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J1

A simple preconcentration neutron activation analysis (PNA) method has been developed for the determination of low levels of iodine in biological and nutritional materials. The method involves dissolution of the samples by microwave digestion in the presence of acids in closed Teflon bombs and preconcentration of total iodine, after reduction to iodide with hydrazine sulfate, by coprecipitation with bismuth sulfide. The effects of different factors such as acidity, time for complete precipitation, and concentrations of bismuth, sulfide, and diverse ions on the quantitative recovery of iodide have been studied. The absolute detection limit of the PNA method is 5 ng of iodine. Precision of measurement, expressed in terms of relative standard deviation, is about 5% at 100 ppb and 10% at 20 ppb levels of iodine. The PNA method has been applied to several biological reference materials and total diet samples.

### INTRODUCTION

Iodine is considered an essential element. The daily dietary safe and adequate intake range of iodine for adults is reported to be 150-200  $\mu\text{g}$  (1, 2). Excessive iodine intake can contribute to certain thyroid disorders in susceptible individuals. In many countries, regulations require the control of the level of daily iodine intake through diet. The accurate determi-

nation of iodine in materials such as diets, excreta, and tissues is of much interest in medical, nutritional, and epidemiologic research.

The analytical techniques most commonly employed for measuring iodine levels are colorimetry (3, 4), ion-selective electrode (5-7), isotope exchange (4, 8), gas chromatography (2, 9), and neutron activation analysis (NAA). The last technique has an excellent intrinsic sensitivity for iodine. However, low levels of iodine in biological materials cannot be easily measured by conventional reactor-flux instrumental NAA (INAA) because of interferences from the high activities of thermal neutron activation products of Na, K, Mn, Br, and Cl which are generally present in high amounts. Epithermal INAA (EINAA) can reduce some of these interferences but does not eliminate them completely. Thermal INAA involving combustion and gas-phase separation of iodine on hydrated manganese dioxide has been applied to determine iodine in biological (10) and total diet (11) samples. Applications of EINAA methods using boron, cadmium, and some combinations of boron and cadmium as thermal neutron shields to biological and geological materials have been reported (12-19). The EINAA methods have been applied for the analysis of iodine in milk (20, 21), infant formula (22), blood (23), biological reference materials (24-28), and food samples (29). Radiochemical NAA (RNAA) has been employed for the estimation of iodine in plant material (30), reference materials (31-33), and rock samples (34).