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The Preparation and Properties of the Manganese(II) Ion-Selective Electrode

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For the measurement of manganese(II)-ion activity, manganese(II) ion-selective electrodes were prepared and tested. As electrodes, heterogeneous membranes were prepared by dispersing sensitive materials, such as manganese sulfide, manganese borate, or manganese dibenzyldithiocarbamate, in silicone rubber, poly(vinyl chloride), or poly(vinyl acetate). A manganese chloride solution (0.1 mol dm^{-3}) was used as the internal reference solution, along with an Ag/AgCl internal reference electrode. The manganese(II) ion-selective electrodes thus made were then examined in terms of their response curves, response times, the effect of the pH, the variation in the response slopes with the temperature, and selectivity coefficients. The response time of the manganese dibenzyldithiocarbamate electrode was within 15 s in the concentration range of 10^{-8}—10^{-1} mol dm^{-3}. The response slope was 33.14 mV/pMn^{2+} in the linear part, and the coefficient of correlation was 0.999. The selectivity coefficients were examined by the separate-solution method.

In recent years, a number of books[1-3] and review articles[4-7] on various aspects of ion-selective electrodes have appeared. In spite of great recent progress in the study of ion-selective electrodes, however, very few manganese(II) ion-selective electrodes have been developed.[8-10] To measure the manganese-ion activity, several manganese(II) ion-selective electrodes have been prepared and tested.

Experimental

Apparatus and Reagents. A digital pH/mV meter, Model PT 3D (Toyo Kagaku Sangyo Co., Ltd.), was used to make the potential measurements (Fig. 1). All the reagents were of an analytical-reagent grade(Wako Pure Chemical Industries). Redistilled water was used in all experiments.

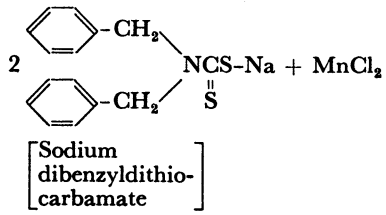
Manganese(II) Ion-Selective Electrode Preparation. Sensitive materials were synthesized as shown below. Manganese sulfide (type α) was formed by the addition of ammonium sulfide to manganese chloride and heated as Eq. 1. Manganese sulfide (type β+γ) was formed by the addition of hydrogen sulfide as in Eq. 2. Manganese hydrogenorthoborate was obtained by the addition of borax to manganese sulfate, while manganese dibenzyldithiocarbamate was obtained by the addition of sodium dibenzyldithiocarbamate to manganese chloride, as in Eqs. 3 and 4 respectively.

$$(NH_4)_2S + MnCl_2 = MnS \text{ (type } \alpha) + 2NH_4Cl \quad (1)$$

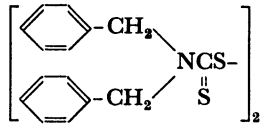
$$H_2S + MnCl_2 = MnS \text{ (type } \beta+\gamma) + 2HCl \quad (2)$$

$$Na_2B_4O_7 + 2MnSO_4 + 5H_2O = 2MnH_4(BO_3)_2 + 2NaHSO_4 \quad (3)$$

(Borax) [Manganese hydrogen-orthoborate]



[Sodium dibenzyldithio-carbamate]



(4)

[Manganese dibenzyldithio-carbamate]

The analytical data on manganese dibenzyldithiocarbmate are shown in Table 1. The analytical data agree reasonably well with the calculated values.

Heterogeneous membranes were prepared with these manganese salts by using, at room temperature, vulcanized silicone rubber (Toshiba RTV silicone rubber), poly(vinyl

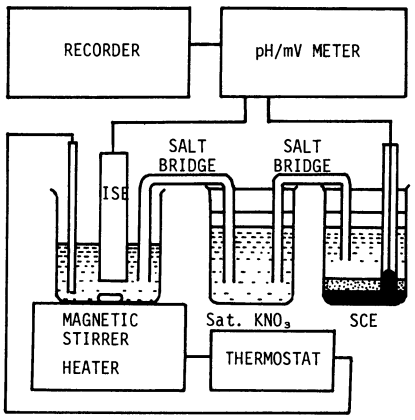


Fig. 1. Apparatus for measurement of potential.

Table 1. Ultimate Analysis of Manganese Dibenzyldithiocarbamate

	H(%)	C(%)	N(%)	Ash(%)
Calcd	4.71	60.08	4.67	9.16
Found	4.54	58.64	4.53	10.41

chloride), or poly(vinyl acetate) as the matrix in a weight ratio of manganese salt to the matrix of 1 to 4. The membranes were left to stand in the air for at least 12 h. Then a suitable section (a circle with a radius of 7 mm) of the membranes was attached to the end of the glass tubing with epoxy-resin-series adhesive. A solution of 0.1 mol dm^{-3} manganese chloride was used as the internal reference solution. Finally the silver-silver chloride electrode was inserted. The manganese(II) ion-selective electrodes were conditioned in a 0.1 mol dm^{-3} manganese chloride solution for 12-h periods and then stored at room temperature in a 0.1 mol dm^{-3} manganese chloride solution. The structure of the manganese(II) ion-selective electrode is shown in Fig. 2.

An electrochemical cell is as follows:

$$\underbrace{\oplus Ag|AgCl,\ Mn^{2+},\ Cl^-|\begin{matrix}\text{Activity}\\ \text{Sensitive}\\ \text{Material}\end{matrix}}_{\text{Manganese(II) ion-selective electrode}}$$

$$\underbrace{|Mn^{2+},Cl^-|}_{\text{Sample solution}}\underbrace{|K^+,\ Cl^-,\ AgCl|Ag\ominus}_{\text{Reference electrode}}$$

Results and Discussion

Response Curve. The responses of 10 manganese ion-selective electrodes were examined. The manganese-ion activity was calculated by means of the Debye-Hückel limitting equation. Figure 3 shows the response of a manganese(II) ion-selective electrode, with manganese sulfide (type α) as the sensing material. The slope of the E vs. manganese-ion activity was 28.49 mV/decade in the linear part of 10^{-4} to 10^{-1} mol dm^{-3}, and the coefficient of correlation was 0.998. Figure 4 shows the response of a manganese(II) ion-selective electrode with manganese dibenzyldithiocarbamate. The slope of the E vs. manganese-ion activity was 33.14 mV/decade in the linear part of 10^{-6} to 10^{-1} mol dm^{-3}, and the coefficient of correlation was 0.999.

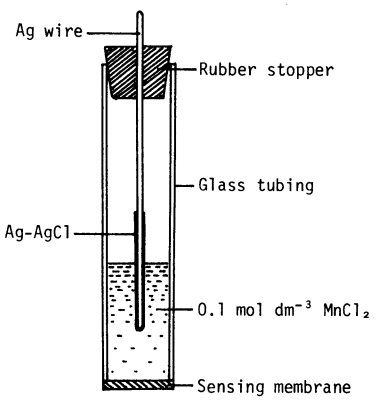


Fig. 2. Manganese(II) ion-selective electrode.

Response Slope. The response slopes of manganese(II) ion-selective electrodes are summarized in Table 2. The response slopes of manganese sulfide (type α) in silicone rubber, manganese sulfide (type β+γ) in silicone rubber, manganese sulfide (type β+γ)-silver sulfide in poly(vinyl acetate), and manganese dibenzyldithiocarbamate in silicone rubber are close to the Nernstian slope (29.57 mV/decade at 25 °C). With these electrodes, the slopes of E vs. the manganese-ion activity in the linear parts were 28.49 mV/decade, 28.52 mV/decade, 28.85 mV/decade, and 33.14 mV/decade respectively. The lower limits of the linear range were 10^{-4} mol dm^{-3} for the electrode with manganese sulfide (type α) in silicone rubber, manganese sulfide (type β+γ) in silicone rubber, and manganese sulfide (type β+γ)-silver sulfide in poly(vinyl acetate), and 10^{-6} mol dm^{-3} for the electrode with manganese dibenzyldithiocarbamate in silicone rubber.

Response Time. The response times (according to the definition of IUPAC[11]) of the manganese(II) ion-selective electrodes were also considered (Figs. 5 and 6). The response times of the electrodes with manganese sulfide (type α) were within 15 s in

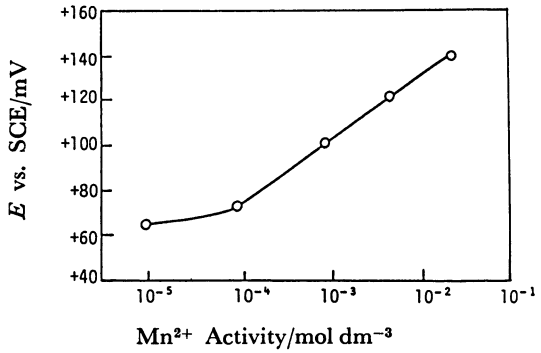


Fig. 3. Response of manganese(II) ion-selective electrode [manganese sulfide (type α)] to manganese ion.

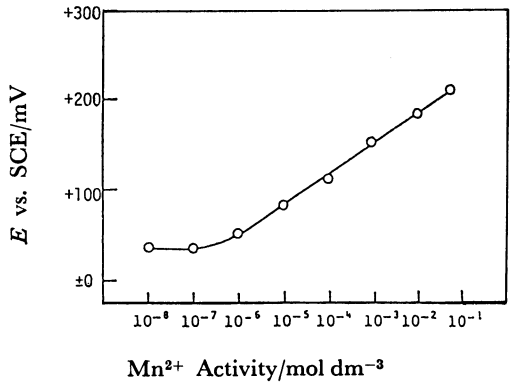


Fig. 4. Response of manganese(II) ion-selective electrode (manganese dibenzyldithiocarbamate) to manganese ion.

Table 2. Response Slopes and Coefficients of Correlation of Manganese(II) Ion-Selective Electrodes

Activity-sensitive material	Matrix	Response slope (mV/pMn^{2+})	Linear part (pMn^{2+})	Coefficient of correlation
MnS(α)	Silicone rubber	28.49	1—4	0.998
MnS(α)	Poly(vinyl chloride)	46.13	1—4	0.994
MnS(β+γ)	Silicone rubber	28.52	1—4	0.990
MnS(α)+Ag_2S	Silicone rubber	21.16	1—3	0.998
MnS(β+γ)+Ag_2S	Poly(vinyl acetate)	28.85	1—4	0.994
MnS(α)+C	Silicone rubber	6.61	1—3	0.981
$MnH_4(BO_3)_2$	Silicone rubber	22.44	1—3	1.000
Dowex 50W-X8	Silicone rubber	23.14	1—4	0.985
Amberlite CG-120	Silicone rubber	4.71	2—4	0.999
$[(C_6H_5\cdot CH_2)_2NCS_2]_2Mn$	Silicone rubber	33.14	1—6	0.999

Table 3. Selectivity Coefficients of Manganese(II) Ion-Selective Electrodes

Interfering ion	Selectivity coefficient[a]			
	MnS(α) electrode	MnS(β+γ) electrode	MnS(β+γ)-Ag_2S electrode	$[(C_6H_5\cdot CH_2)_2NCS_2]_2Mn$ electrode
Zn^{2+}	7.5×10^{-1}	9.9×10^{-1}	6.7×10^{-1}	5.8×10^{-3}
Cu^{2+}	4.7×10^{-1}	1.7	1.5	6.3×10^{-3}
Ni^{2+}	2.2	1.7	9.7×10^{-1}	1.3×10^{-2}
Cr^{3+}	5.3	6.7	4.2	6.8×10^{-3}
Pb^{2+}	3.1	3.0	9.7×10^{-1}	1.6×10^{-2}
Cd^{2+}	7.5	4.3	1.6	9.4×10^{-3}
Mg^{2+}	5.4×10^{-1}	5.4×10^{-1}	1.2	
Ca^{2+}	9.5×10^{-1}	8.8×10^{-1}	1.0	2.1×10^{-2}
Na^{+}	5.3×10^{-2}	9.2×10^{-2}	1.4×10^{-1}	2.6×10^{-3}
K^{+}	4.6×10^{-2}	6.6×10^{-2}	4.7×10^{-2}	4.2×10^{-2}
Al^{3+}				8.6×10^{-3}

a) Separate-solution method. The selectivity coefficients were calculated from the e.m.f. of a solution containing the manganese(II) ion, at activity 10^{-2} mol dm^{-3}, and a solution containing the interfering ion, at activity 10^{-2} mol dm^{-3}.

the concentration range of 10^{-3}—10^{-1} mol dm^{-3}, 1 min in 10^{-4} mol dm^{-3}, and 2 min in 10^{-5} mol dm^{-3}. The response time of the electrode with manganese dibenzyldithiocarbamate was within 15 s in the concentration range of 10^{-8}—10^{-1} mol dm^{-3}.

Effect of pH. Figure 7 shows the results obtained when the manganese ion was determined with a manganese(II) ion-selective electrode (manganese dibenzyldithiocarbamate) in solutions of various pH values obtained by adding nitric acid or sodium hydroxide. Manganese ions could be determined accurately at pH 2.5—5.5.

The Variation in the Response Slopes with the Temperature. The variation in response slopes with the temperature were also considered (Fig. 8). Over the range of 0—60 °C, the 10^{-2} mol dm^{-3} manganese ion could be determined with the manganese(II) ion-selective electrode [manganese sulfide (type α)]. The experimental value of 0.1095 mV/decade per 1 °C was in good agreement with the calculated value of 0.09922 mV/decade per 1 °C. Similar results were obtained with an electrode with manganese dibenzyldithiocarbamate.

Selectivity Coefficient. The selectivity coefficients of manganese(II) ion-selective electrodes to the several ions, such as the zinc ion, the copper ion, the nickel ion, the chromiun ion, and the lead ion, were examined by means of the separate-solution method (Table 3). The selectivity coefficients were calculated by the separate-solution method from the following relationship:

$$\log K_{MN}=\frac{E_2-E_1}{2.303RT/2F}$$

K_{MN} : Selectivity coefficient
E_1 : Electrode potential in the presence of the M ion
E_2 : Electrode potential in the presence of the N ion
M : Manganese ion
N : Interfering ion
R : Gas constant
T : Absolute temperature
F : Faraday's constant

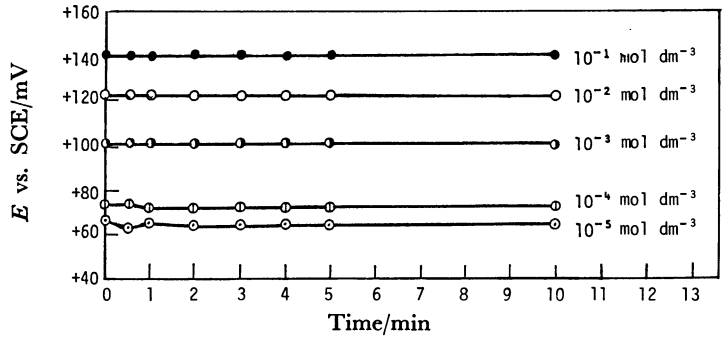


Fig. 5. Response time of manganese(II) ion-selective electrode [manganese sulfide (type α)].

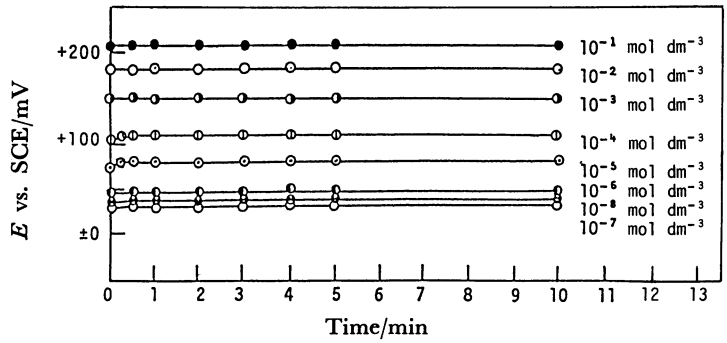


Fig. 6. Response time of manganese(II) ion-selective electrode (manganese dibenzyldithiocarbamate).

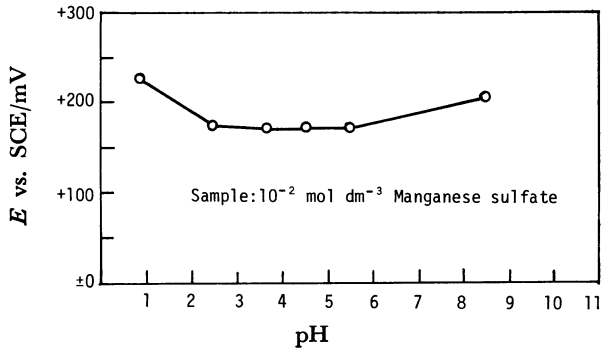


Fig. 7. Effect of pH on manganese(II) ion-selective electrode (manganese dibenzyldithiocarbamate).

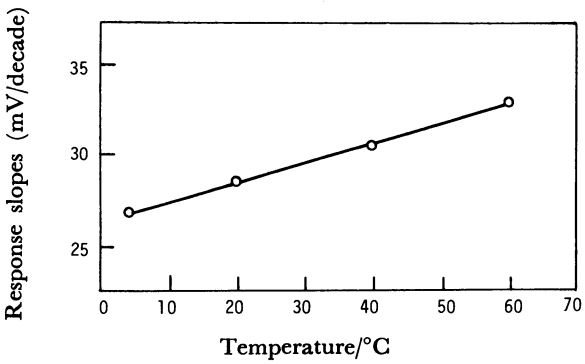


Fig. 8. The variation of response slopes by temperature on manganese(II) ion-selective electrode [manganese sulfide (type α)].

Four types of manganese(II) ion-selective electrodes [manganese sulfide (type α), manganese sulfide (type β+γ), manganese sulfide (type β+γ)-silver sulfide, and manganese dibenzyldithiocarbamate] were tested. The selectivities for monovalent cations (the sodium ion and the potassium ion) were better than those of divalent cations with the manganese sulfide (type α) and manganese sulfide (type β+γ) electrodes. The selectivity coefficients, 2.6×10^{-3}—4.2×10^{-2}, for interfering ions were obtained when the manganese dibenzyldithiocarbamate electrode was used. The electrode potentials were reproducible within 3 mV in 7—10 replicate runs.

References

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