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**General rules for ion selective
electrode method**

ICS 71.040.40

Descriptors : ionization, iodometry, instructions for use, ions, concentration
(chemical), determination of content

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Foreword

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of International Trade and Industry through deliberations at Japanese Industrial Standards Committee in accordance with the Industrial Standardization Law:

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General rules for ion selective electrode method

1 Scope This Japanese Industrial Standard specifies the general matters according to which the ion concentration of organic substance or inorganic substance is measured using an ion selective electrode. Provided that this shall not be applicable to pH measurement.

Remarks 1 The normative references to this Standard are listed in Attached Table 1.

2 The unit dm^3 used in this Standard equals to l , and cm^3 to ml .

2 Generals in common Generals in common shall conform to JIS K 0050.

3 Definitions For the purpose of this Standard, the definitions in JIS K 0211, JIS K 0213, and JIS K 0215 apply, and the rest of the terms are as follows.

- (1) **ion selective electrode** Electrode generating electric potential in response to the activity of special ion in solution.
- (2) **activity** A sort of thermodynamic mass-molar concentration which is given with relation to chemical potential of a chemical species.
- (3) **activity coefficient** This is a ratio of the activity of a chemical species to the concentration, and is the measure by which the deviation of chemical species from the ideal behavior can be expressed.
- (4) **ionic strength** The value given by the formula $1/2 \sum Z_M^2 C_M$, where, C_M is the molar concentration of ionic species M in solution, and Z_M is ionic charge number. Otherwise, the value similarly defined using mass molar concentration.
- (5) **response potential** Electric potential measured on an ion selective electrode when a reference electrode is set as a counter electrode.
- (6) **response slope** The electric potential (mV/concentration difference by ten times) measured when the concentration ratio between two reference solutions.
- (7) **response time** Duration necessary until response potential will get defined indicated value that is stable.
- (8) **selectivity coefficient** The value achieved experimentally which expresses the degree of influence given to the target ion for measurement by coexisting ion.
- (9) **membrane electrode** The electrode system composed of various selective membrane and the electrode installed inside selective membrane.

Remarks In many cases, the membrane electrode is installed by setting an internal reference electrode and electrolyte solution inside selective membrane.

- (10) **glass membrane electrode** Ion sensitive electrode of which sensitive membrane is composed of such glass membrane as $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system or $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system.
- (11) **solid-state membrane electrode** Ion selective electrode of which selective membrane is composed of single crystal of hardly-soluble metal salt or of the membrane that was shaped by moulding with pressure the powder mainly made of hardly-soluble

metal salt.

- (12) **liquid membrane electrode** Ion selective electrode of which selective membrane is composed of high molecular substance impregnated with liquid type ion exchanger that was dissolved in oil-dissolvable organic solvent.
- (13) **gas-selective membrane electrode** The electrode for measuring special gas component which was prepared, after combining pH electrode or ion selective electrode with a reference electrode, by means of covering the combined and internal liquid with gas permeable membrane.
- (14) **reference electrode** The electrode whose electric potential is stabilized and is known comparing with standard hydrogen electrode. It can be used as a counter electrode to control or measure the potential of ion selective electrode.
- (15) **ion meter** The device for measuring the concentration of ion species in solution using an ion selective electrode.
- (16) **ionic strength control solution** Highly concentrated electrolyte solution which is to be added for keeping ionic strength in solution constant.

4 Principle for measurement The ion selective electrode has a sensitive membrane which responds to ion, and when this membrane contacts with specified ion in solution, there takes place membrane electric potential corresponding to the ionic activity. Owing to connecting the reference electrode immersed in sample solution as a counter electrode for ion selective electrode with the d.c. potentiometer with high resistance, this membrane electric potential can be measured, but this relative electric potential, which has been measured by potentiometer, is called a response potential.

The relation between response potential E and ionic activity a to be measured in sample solutions is expressed as shown in formula (1), which is called Nernst equation.

$$E = E_0 + \frac{2.303RT}{ZF} \cdot \log a \quad \dots\dots\dots (1)$$

In this equation, E_0 is standard electrode potential at 25 °C, R is gas constant, T is absolute temperature, Z is number of ionic valence, F is Faraday constant, and $\log$ means the symbol of common logarithms. The value of $2.303RT/ZF$ in Formula 1 is called Nernst constant, and the value of this constant given when the ionic activity is changed by 10 times is called a theoretical response slope. For instance, the theoretical response slope for monovalent ion is 59.16 mV at 25 °C, and the slope for bivalent ion is 29.58 mV. There is a formula (2) showing the relation between ionic activity a and ionic concentration C with an activity coefficient γ , but when generally low concentrated solution, whose total ionic concentration is 10^{-3} (mol/dm³) or lower, is treated, it would be regarded that activity is nearly equal to concentration ($\gamma \approx 1$).

$$a = \gamma C \quad \dots\dots\dots (2)$$

In case of measurement using an ion selective electrode, practically the formula (1) can be expressed as the formula (3) using a really measured response slope S and concentration C .

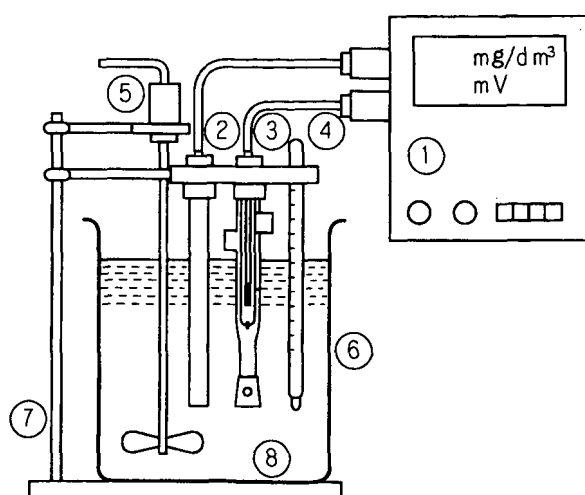
$$E = E_0 + S \cdot \log C \quad \dots\dots\dots (3)$$

In case of general measurement using ion selective electrode, if, employing several

known concentrated solutions with different concentration, the relation between ionic concentration C and response electric potential E has been previously calculated by formula (3), the ionic concentration C in the sample solution could be determined from the response potential E .

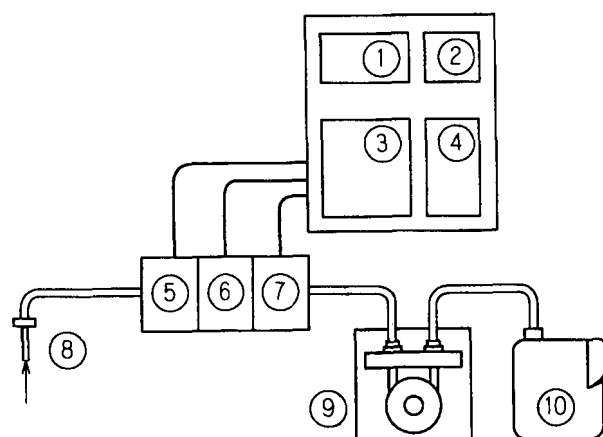
5 Apparatus Making use of d.c. potentiometer of high resistance equipped with an amplifier of electric voltage and display part, ion meter or others, the ionic concentration in water solution can be measured using an ion selective electrode and reference electrode as counter electrode.

5.1 Outline of apparatus The apparatus is composed of a potentiometer or ion meter, ion selective electrode, reference electrode, a sample container, stirrer, and so on. The example of the fundamental construction is shown in Fig. 1 (batch type) and Fig. 2 (flow type).



- ① Potentiometer or ion meter
- ② Ion selective electrode
- ③ Reference electrode (double liquid junction)
- ④ Thermometer
- ⑤ Stirrer
- ⑥ Sample container
- ⑦ Stand for electrode
- ⑧ Sample

Fig. 1 Example of batch-type measuring apparatus using ion selective electrode



- ① Display
- ② Printer
- ③ Signal amplifier (including analog/digital signal transducer)
- ④ Controller (including signal processor)
- ⑤ Ion electrode A
- ⑥ Ion electrode B
- ⑦ Reference electrode
- ⑧ Aspirator nozzle
- ⑨ Pump
- ⑩ Tank for wastewater

Fig. 2 Example of flow-type measuring apparatus using ion selective electrode

5.2 Measuring apparatus

(1) Type

- (a) **potentiometer** D.C. potentiometer with high input resistance ($10^{12} \Omega$ or more) for measuring the response potential of ion selective electrode. The response potential shall be converted into ionic concentration by either graphing or data processing.

For instance, there is a digital pH-mV meter or pH-mV meter with magnified scale.

- (b) **ion meter** Device to measure the response potential of ion selective electrode and then convert it into the concentration scale.

For instance, there is a analog-type or digital-type ion meter (with mg/dm^3 , mol/dm^3 scale).

(2) Uses

- (a) **for laboratory or portable use** There is an ion meter exclusively usable for sodium ion, fluoride ion, cyanide ion, or others.
- (b) **for ion monitor** There are exclusively monitors such as ion monitor for cyanides, ion monitor for chlorides, ion monitor for fluorides, ion monitor for sodium ion, or other various ion monitors which were installed in an automatic monitoring device for water quality.
- (c) **for clinical examination** These devices are installed in an automatic analyzer for examining a specimen such as blood.

Some automatic analyzer can measure such as sodium ion, potassium ion, chloride ion, lithium ion, existing in blood.

- (d) **for flow injection analyzer** This can be used for detector in the flow injection analysis, and can determine ionic concentration.
- (e) **for flue gas monitor** This can be used for measuring components in flue gas. There is a monitor for hydrogen chloride gas.

5.3 Type of ion selective electrodes These electrodes shall have membrane which has ion selectivity and can generate electric potential depending on ionic concentration, and are classified into glass membrane electrode, solid-state membrane electrode, liquid membrane electrode, and gas-selective membrane electrode according to the kind of sensitive membrane. The examples of main ion selective electrodes are shown in Table 1, and their constructions are shown in Fig. 3.

5.4 Type of reference electrode There are a single liquid junction type and double liquid junction type, depending on the shape of an electrode, and in its inside such as silver-silver chloride electrode or calomel [mercury-mercury (I) chloride electrode] is used. The liquid junction is classified into sleeve type or ceramic type by its shape. The constructions of main reference electrodes are exemplified in Fig. 4.

Table 1 Examples of types of ion selective electrodes

Ion selective electrode to be used	Type of electrode	Kind of electrode	Approximate range of determination		Response slope (mV/concentration change by 10 times)	Measurable range of pH	Main disturbing ions
			mg/dm ³	mol/dm ³			
Glass membrane electrode	Solid-state membrane electrode	Na ⁺	0.2 to 23 000	10 ⁻⁵ to 10 ⁰	50 to 60	6 to 11	Ag ⁺ , H ⁺
		Cl ⁻	2 to 35 000	5 × 10 ⁻⁵ to 10 ⁰	-50 to -60	2 to 11	S ²⁻ , CN ⁻ , S ₂ O ₃ ²⁻ , Br ⁻
		Br ⁻	0.1 to 80 000	10 ⁻⁶ to 10 ⁰	-50 to -60	2 to 12	S ²⁻ , CN ⁻
		I ⁻	0.1 to 13 000	10 ⁻⁶ to 10 ⁻¹	-50 to -60	3 to 12	S ²⁻ , CN ⁻
		CN ⁻	0.03 to 260	10 ⁻⁶ to 10 ⁻²	-50 to -60	11 to 13	S ²⁻ , I ⁻
		S ²⁻	0.03 to 32 000	10 ⁻⁶ to 10 ⁰	-25 to -30	13 to 14	
		Ag ⁺	0.01 to 100 000	10 ⁻⁷ to 10 ⁰	50 to 60	2 to 9	Hg ²⁺
		Pb ²⁺	0.2 to 20 000	10 ⁻⁶ to 10 ⁻¹	25 to 30	4 to 7	Hg ²⁺ , Ag ⁺ , Cu ²⁺ , Fe ³⁺ , Cd ²⁺ , Cl ₂
		Cd ²⁺	0.01 to 11 000	10 ⁻⁷ to 10 ⁻¹	25 to 30	3 to 7	Hg ²⁺ , Ag ⁺ , Cu ²⁺ , Fe ³⁺ , Pb ²⁺ , Cl ₂
		Cu ²⁺	0.01 to 6 000	10 ⁻⁷ to 10 ⁻¹	25 to 30	3 to 7	Hg ²⁺ , Ag ⁺
Solid-state membrane electrode (single crystal)		F ⁻	0.02 to 20 000	10 ⁻⁶ to 10 ⁰	-50 to -60	5 to 8	Al ³⁺ , Fe ³⁺ , Ca ²⁺ , OH ⁻
Liquid membrane electrode		Cl ⁻	3 to 3 500	10 ⁻⁴ to 10 ⁻¹	-50 to -60	3 to 10	ClO ₄ ⁻ , I ⁻ , Br ⁻ , NO ₃ ⁻
		NO ₃ ⁻	6 to 6 000	10 ⁻⁴ to 10 ⁻¹	-50 to -60	3 to 10	ClO ₄ ⁻ , I ⁻
		Li ⁺	0.1 to 700	10 ⁻⁵ to 10 ⁻¹	50 to 60	3 to 10	K ⁺ , Na ⁺ , Cs ⁺
		Na ⁺	0.2 to 20 000	10 ⁻⁵ to 10 ⁰	50 to 60	3 to 10	K ⁺
		K ⁺	0.4 to 4 000	10 ⁻⁵ to 10 ⁻¹	50 to 60	3 to 10	Cs ⁺
		NH ₄ ⁺	0.2 to 18 000	10 ⁻⁵ to 10 ⁰	50 to 60	4 to 8	K ⁺ , Na ⁺
		Ca ²⁺	0.4 to 4 000	10 ⁻⁵ to 10 ⁻¹	25 to 30	5 to 8	Zn ²⁺
		Bivalent cation	0.4 to 4 000	10 ⁻⁵ to 10 ⁻¹	25 to 30	5 to 8	
Gas-selective membrane electrode		NH ₃	0.03 to 170	2 × 10 ⁻⁶ to 10 ⁻²	-50 to -60	11 to 13	Volatile amines
		CO ₂	4 to 440	10 ⁻⁴ to 10 ⁻²	50 to 60	0 to 4	NO ₂ , SO ₂ , CH ₃ COO ⁻
		NO ₂	0.2 to 460	5 × 10 ⁻⁶ to 10 ⁻²	50 to 60	0 to 1	CO ₂ , CH ₃ COO ⁻

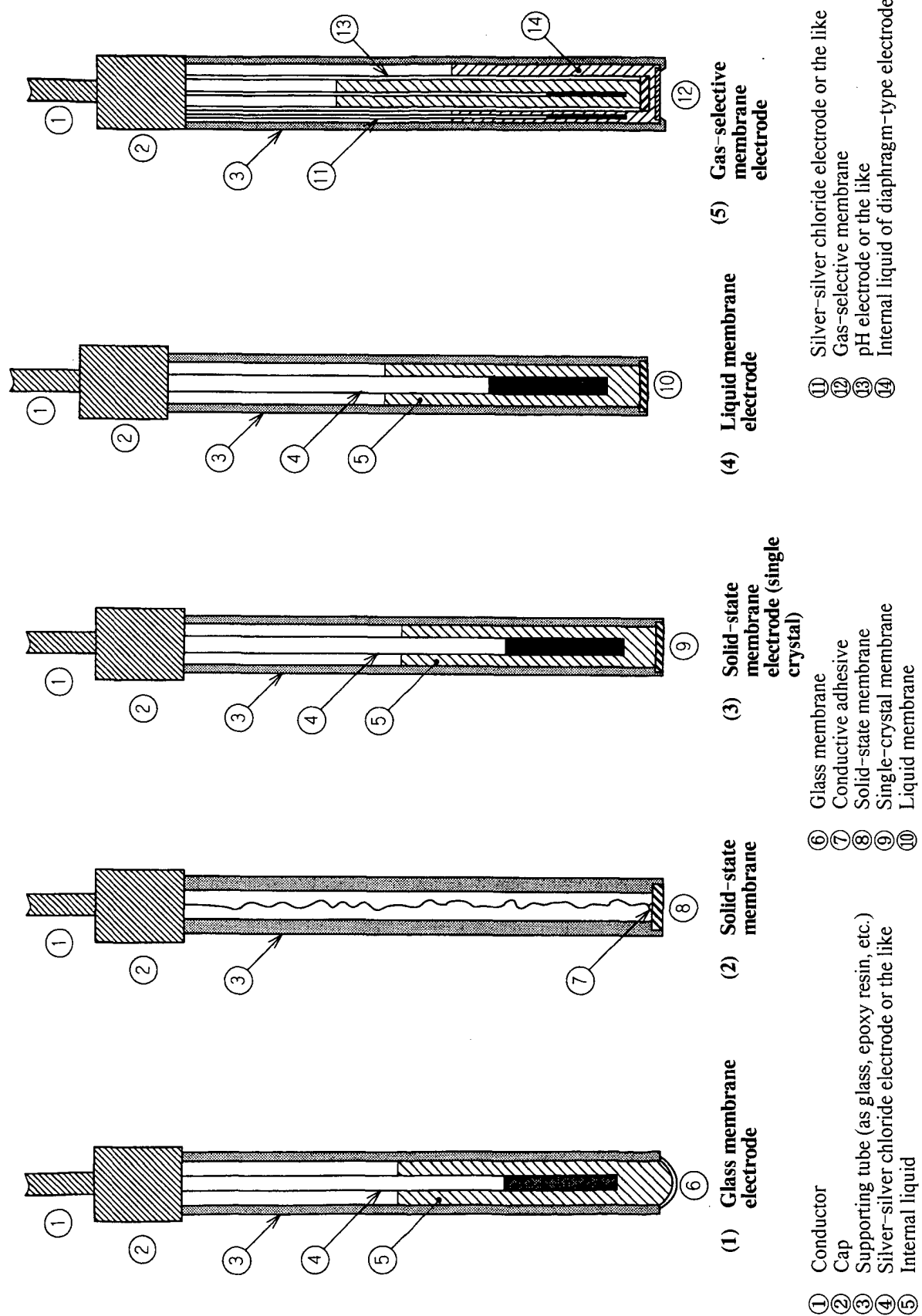


Fig. 3 Examples of constructions of ion selective electrodes