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Some Characteristics of Ion-Selective Electrodes

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Abstract

Some physicochemical characteristics of commercially available ion-selective electrodes were investigated in order to assess factors which might limit their performance in analytical chemistry.

Limitations depend upon the values of the time response, precision, and the temperature coefficient, including the effects of variation in room temperature. All values were determined for pure standard solutions and for those of constant ionic strength over the concentration ranges of $1 \times 10^{-2} \text{ M}$ to the lower detection limit. Using electrodes from three leading manufacturers (Orion, Beckman, and Corning), the measurements showed that the characteristics could not be attributed to differences in construction but were due to differences between individual electrodes.

Résumé

Dans ce rapport, l'auteur étudie quelques caractéristiques physico-chimiques des électrodes sélectives d'ions disponibles dans le commerce. Le but de cette étude est d'évaluer les facteurs qui pourraient limiter l'usage de ces électrodes en chimie analytique.

Les limitations paraissent dépendre de la rapidité avec laquelle ces électrodes réagissent, de leur précision, du coefficient de température ainsi que des effets de la variation de la température ambiante. La totalité des valeurs de temps de réaction a été déterminée pour des solutions standard pures et pour des solutions ayant une concentration ionique constante comprise entre $1 \times 10^{-2} \text{ M}$ et l'ultime limite inférieure de détection. Les mesures, utilisant les électrodes fournies par les trois fabricants d'avant-garde (Orion, Beckman, Corning) montrent que les caractéristiques ne peuvent pas être attribuées à des différences de conception mais plutôt aux différences entre les électrodes elles-mêmes.

Some Characteristics of Ion-Selective Electrodes

Ivan Šekerka and Josef F. Lechner

INTRODUCTION

The most common application of ion-selective electrodes is in direct potentiometric measurement, where the measured cell potential is directly related to the activity of the ion in the solution (Durst, 1969). Ion-selective electrodes are used to measure the concentration of an ion of particular interest by making use of such methods as single known addition (Orion Research, 1969) or double known addition (Orion Research, 1970a), subtraction (Orion Research, 1970b), analate addition and subtraction (Orion Research, 1970c). The application of these electrodes is of specific interest in water quality and pollution measurements, since they offer a fast and simple method of determining some of the common ions. These devices are relatively inexpensive, and when used with proper understanding of their characteristics, the results are as accurate as those obtained by the conventional analytical techniques (Riseman, 1969; Andelman, 1968).

Although the theory, operation, application, and the analytical usefulness of these electrodes has already been presented for a number of systems, many problems in their application for routine analytical purposes remain unresolved (Frant *et al.*, 1968; Smrček *et al.*, 1958; Eisenman, 1969; Ross, 1969; Pungor, 1967, and Light, 1969). The following data, for example, are not satisfactorily covered in the literature:

- i) time of response
- ii) precision
- iii) stability of the potential over a long time period
- iv) effect of the temperature
- v) effect of the room temperature and light intensity.

The present paper discusses these characteristics for different types of ion-selective electrodes.

EXPERIMENTAL

Reagents

All chemicals were of reagent grade. Double-distilled water was used for all solutions.

Apparatus

The ion-selective electrodes listed in Table 1 were used in this study and were prepared according to the manufacturer's directions. All data herein reported were obtained with the Orion 801 digital pH/mV meter, the Orion 855 six-channel automatic switch, the Orion 851 digital printer system and the Hewlett-Packard 7004A recorder. The constant signal source was a Keithley 260 nanovolt secondary standard. The solution temperature

TABLE 1. Types of ion-selective electrodes

	Orion	Beckman	Corning
Chloride	94-17	39604	
Bromide	94-35	39602	
Iodide	94-53	39606	
Sulphide	94-16	39610	476129
Cyanide	94-06		
Cupric	94-29		476133
Lead	94-82		
Cadmium	94-48		
Fluoride	94-09	39600	476042
Sodium	94-11		476210
Calcium	92-20		476041
Divalent cation	92-32		476235
Potassium	92-19		476132
Fluoroborate	92-05		
Nitrate	92-07		476134
Chloride	92-17		476131
Perchlorate	92-81		

was maintained with a Haake K42 circulating thermostated water bath, and the air temperature with a Lab-line Imperial II incubator. Single-junction Orion 90-01 or double-junction Orion 90-02 electrodes were used as reference electrodes immersed directly into the solution or with an intermediate electrolytic bridge. The apparatus and its component parts are shown schematically in Figure 1. The stirring was identical and constant for all measurements. The estimation of the influence of light intensity on the ion-selective electrode potential was accomplished with the help of a microscopic illuminator using a variable voltage source to achieve the changes of light intensity. The light was focused directly onto the surface of the ion-selective electrode crystal. A more accurate measurement of this phenomenon would be beyond the range of this study.

The measurements were conducted in pure standard solutions as well as in the presence of total ionic strength adjusters and in the concentration ranges of $1 \times 10^{-2} \text{ M}$ to the lower detection limit of the electrode. For an electrode responding to univalent ion, an overall error of 1 mV corresponds to a 3.9% relative error in activity and for an electrode sensing divalent ion, the relative error is 7.8% per 1 mV.

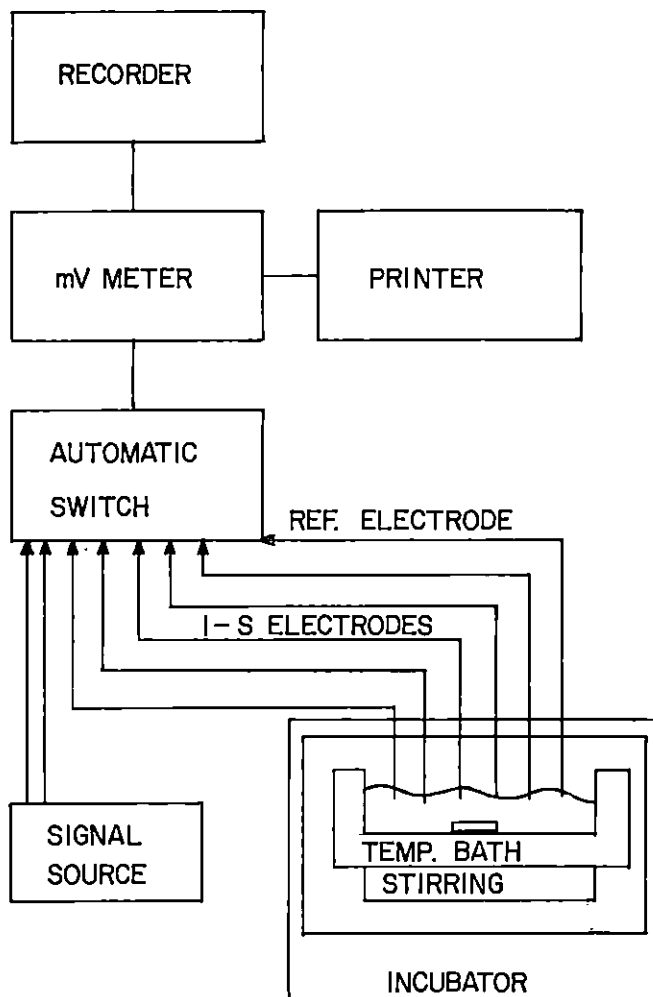


Figure 1. Apparatus for measuring characteristics of ion-selective electrodes.

RESULTS

Time Response

The time period was measured during which the initial electrode potential was unstable and changed to a relatively constant value. The point dividing the area of the instability and the relatively stable potential, was derived from the recorded potential-time curve as an empirical point from which the electrode potential varied due to the drift of the potential and the noise of the instruments. A typical example of this curve is shown in

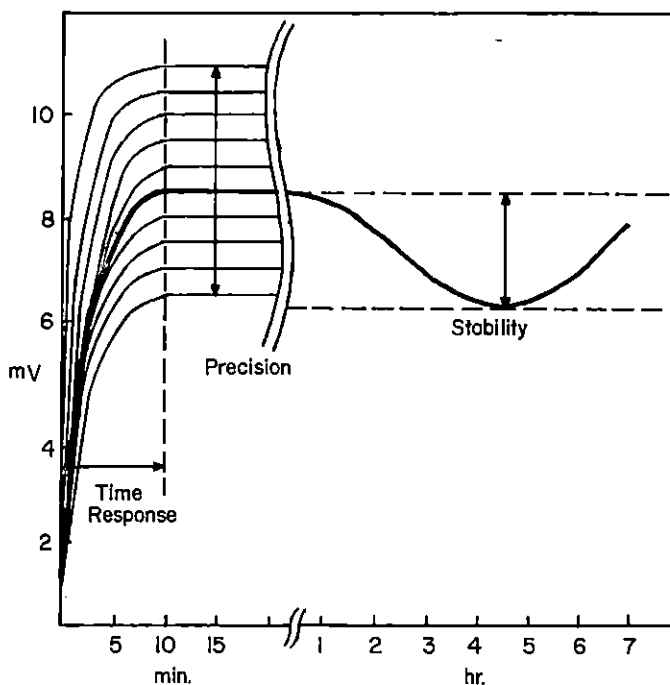


Figure 2. Potential-time curve of an ion-selective electrode.

Figure 2. The speed of response depended very much on the "state of readiness" of the device. Optimum readiness occurred after soaking the electrodes in a nearly similar concentration of the prime ion, resulting in short-time response. Unprepared electrodes taken out of dry storage or electrodes used previously under different conditions have a much slower speed of response. The observed differences in the time responses were probably due to the formation or rebuilding of the active surface layer of the sensing element. It is, therefore, necessary to allow enough time for stabilization of the potential and this time period has to be determined individually for each electrode and its application. In our experiments the electrodes were presoaked in the double-distilled water and the measurements were accomplished with increasing levels of the ion of interest. The results are summarized in Table 2. The time response was reasonably short for the high concentration range and lengthened with the decreasing concentration of the ion of interest. This time period increased very rapidly as the detection limit was approached and measurement became difficult. The electrodes in pure standard solutions and in solutions with constant ionic strength behaved in a similar manner. Practically no difference was found between the electrodes of different manufacturers.

Precision

An important factor in using the ion-selective electrode for direct potentiometric measurements is the precision which can be related to the reproducibility of the measurements. The precision as the concordance of a series of measurements of the same quantity was deter-

TABLE 2. Time response in minutes

Electrode	Manufacturer	Concentration (m)					
		1×10^{-2}	1×10^{-4}	1×10^{-5}	1×10^{-6}	1×10^{-7}	1×10^{-8}
Sulphide	Orion	3	4	5	5	10	15
	Beckman	3	3	5	5	10	15
	Corning	2	4	5	5	10	15
Silver	Orion	2	4	5	5	10	
	Beckman	2	3	5	5	10	
Chloride	Orion	2	5	15			
	Beckman	3	5	20			
Iodide	Orion	6	5	10	10	15	
	Beckman	3	4	5	10	15	
Mercury	Orion	2	2	3	5	10	15
Bromide	Orion	4	5	10	10	20	
	Beckman	3	5	10	10	20	
Cyanide	Orion	5	5	10	15	30	
Fluoride	Orion	1	1	2	3		
	Beckman	1	1	2	3		
	Corning	1	1	2	3		
Cupric	Orion	1	1	1	2	3	5
	Corning	1	1	1	2	5	10
Lead	Orion	2	2	4	10		
Cadmium	Orion	1	1	1	3	5	
Sodium	Orion	2	2	5	10		
	Corning	3	3	5			
Calcium	Orion	2	2	5			
	Corning	2	2	5			
Divalent Cation	Orion	2	2	5			
	Corning	2	2	5			
Potassium	Orion	2	2	2	5		
	Corning	2	2	5	5		
Fluoroborate	Orion	2	2	20			
Perchlorate	Orion	2	2	4			
Nitrate	Orion	3	4	20			
	Corning	3	4	20			
Chloride (liquid exchanger)	Orion	2	2	5			
	Corning	2	2	5			

mined by recording the electrode potential after 10 times repeated immersion (15 min) and withdrawal (15 min) of the electrode. The electrode was blotted dry after each withdrawal. A 15-minute period was used to allow the electrode enough time to reach the relatively stable potential. The results of these measurements are given in Table 3 and indicate a decrease of precision with the decreasing concentration of the ion of interest. Serious limitations of the electrodes' performance were observed close to the detection limits. The precision of the measurements was slightly better in a solution with a constant ionic strength than in a pure standardizing solution. The electrodes of different manufacturers behaved in similar manner.

Stability of the Potential

The stability of the electrode potential over a long time period is the important characteristic of the ion-selective electrode. (This is particularly important for the incorporation into the continuous monitoring system.)

This characteristic — the drift of the mean potential after passing the point limiting the area of the time response — was measured during a six-hour period. The values of the stability expressed in mV are presented in Table 4. The instability of the potential rose markedly in concentrations close to the detection limit, where the drift of the electrode potential limited the use of the electrode. The drift was somewhat smaller in solutions with constant ionic strength than in pure standard solutions. No significant difference was observed between the electrodes of different manufacturers.

Temperature Coefficient

The temperature coefficient, as measured, was the overall effect of changing the temperature of the solution while holding the reference electrode (intermediate electrolytic bridge) at room temperature. This experimental coefficient consisted of the standard temperature coefficient of the solution and the coefficient of the liquid junction potential. A summary of the results is presented

TABLE 3. Precision in \pm mV

Electrode	Manufacturer	Concentration (m)					
		1×10^{-2}	1×10^{-4}	1×10^{-5}	1×10^{-6}	1×10^{-7}	1×10^{-8}
Sulphide	Orion	3	3	2	3	6	10
	Beckman	2	2	2	3	5	10
	Corning	3	3	2	5	5	12
Silver	Orion	3	3	3	4	5	
	Beckman	2	3	3	3	4	
Chloride	Orion	2	3	5	9		
	Beckman	3	3	4	9		
Iodide	Orion	2	3	4	3	5	6
	Beckman	2	2	3	4	4	8
Mercury	Orion	2	2	2	4	5	8
Bromide	Orion	2	2	4	5		
	Beckman	2	3	4	5		
Cyanide	Orion	3	4	6	10		
Fluoride	Orion	1	1	1	2		
	Beckman	1	1	1	2		
	Corning	1	1	1	2		
Cupric	Orion	0.5	0.5	0.5	1	1	1.5
	Corning	0.5	0.5	0.5	1	1.5	1.5
Lead	Orion	0.5	1	1.3	1.5		
Cadmium	Orion	0.5	1	1	1.5	2.5	
Sodium	Orion	2	2	4			
	Corning	2	2	5			
Calcium	Orion	2	3	5			
	Corning	2	2	5			
Divalent cation	Orion	2	3	5			
	Corning	2	2	5			
Potassium	Orion	2	2	3	10		
	Corning	2	2	2	8		
Fluoroborate	Orion	1	1	3			
Perchlorate	Orion	2	3	5			
Nitrate	Orion	2	2	4			
	Corning	2	2	4			
Chloride (liquid exchanger)	Orion	3	3	5			
	Corning	3	4	5			

in Table 5. The temperature coefficient of all ion-selective electrodes in the temperature range of 5–40°C remained practically constant (1.2–1.3 mV/°C). Only in concentration representing the lower detection limit, did the coefficient rise to a value of 1.7 mV/°C. It is important to mention that the dependence of the electrode potential on the temperature was not exactly linear. The potential versus temperature curves possessed a drift, probably due to individual electrode characteristics (long-term change in mean potential) and to the many variable contributions of the potential mentioned above.

Room Temperature and Light Intensity

It was observed that the potential of some ion-selective electrodes was very sensitive to varying room temperature, even though the solution temperature remained constant. For the purpose of illustration, variations in room temperature of $\pm 2^\circ\text{C}$, which are customary in air-conditioned laboratories, may result in a relative error of $\pm 15\%$ in concentrations. The $\text{Ag}_2\text{S}/\text{AgX}$ elec-

trodes (sulphide, silver, chloride, iodide, mercury, bromide and cyanide) were the most sensitive to varying room temperature, having a coefficient $\pm 2\text{mV}/^\circ\text{C}$. The values of the external temperature coefficients of $\text{Ag}_2\text{S}/\text{AgMe}$ electrodes (cupric, lead and cadmium) were in the range of 0.1–0.5 mV/°C. All remaining electrodes were not sensitive to changes in room temperature.

The potentials of $\text{A}_2\text{S}/\text{AgX}$ electrodes were sensitive to changes in light intensity. The change of the electrode potential in our experiments reached values of up to 50 mV. The changes of the potentials of $\text{Ag}_2\text{S}/\text{AgMe}$ electrodes due to varying light intensity were found to be negligible. The other types of ion-selective electrodes were not sensitive to changes in light intensity.

To obtain reproducible results by using $\text{Ag}_2\text{S}/\text{AgX}$ and $\text{Ag}_2\text{S}/\text{AgMe}$ electrodes it is essential that temperature and light intensity in the laboratory be kept at constant levels during calibration and measurement. If constant conditions are not guaranteed, it is necessary to determine and use correction factors.

TABLE 4. Stability of the potential in mV

Electrode	Manufacturer	Concentration (m)					
		1×10^{-2}	1×10^{-4}	1×10^{-5}	1×10^{-6}	1×10^{-7}	1×10^{-8}
Sulphide	Orion	3	2	3	2	5	5
	Beckman	2	2	2	3	4	7
	Corning	2	2	3	3	3	6
Silver	Orion	1	4	4	4	10	
	Beckman	2	3	5	5	10	
Chloride	Orion	1	4	10	17		
	Beckman	1	5	10	18		
Iodide	Orion	2	2	3	3	5	10
	Beckman	2	3	3	5	2	10
Mercury	Orion	2	2	2	3	5	5
Bromide	Orion	2	3	3	7	10	
	Beckman	1	2	3	5	10	
Cyanide	Orion	2	2	2	5		
Fluoride	Orion	1	1	1	1		
	Beckman	1	1	1	1		
	Corning	1	1	1	1		
Cupric	Orion	0.2	0.5	0.5	0.5	2	4
	Corning	0.4	0.5	0.5	1	2	4
Lead	Orion	1	1	1.5	2		
Cadmium	Orion	1	1	1	1.5	2	
Sodium	Orion	2	2	5			
	Corning	2	2	5			
Calcium	Orion	1	1	3			
	Corning	1	2	3			
Divalent cation	Orion	1	1	3			
	Corning	1	2	3			
Potassium	Orion	5	5	10	20		
	Corning	3	4	8	15		
Fluoroborate	Orion	1	1	2			
Perchlorate	Orion	2	2	5			
Nitrate	Orion	1	2	3			
	Corning	1	3	5			
Chloride (liquid exchanger)	Orion	2	3	5			
	Corning	1	3	5			

CONCLUSIONS

From the characteristics measured in the experiments it can be concluded that the fluoride, cupric, cadmium, and calcium electrodes will be superior in application to the other electrodes. It is also obvious that when measurements involving ion-selective electrodes are made, conditions of measurements must be maintained constant if meaningful results are to be obtained.

Although the application of ion-selective electrodes for certain problems is dependent on many factors such as selectivity, sensitivity, detection limit, mode of use, required accuracy etc., the characteristics estimated and presented in this study are of fundamental importance and must be taken into account in any studies involving the use of ion-selective electrodes.

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TABLE 5. Temperature coefficients in mV/°C

Electrode	Manufacturer	Concentration (m)					
		1×10^{-2}	1×10^{-4}	1×10^{-5}	1×10^{-6}	1×10^{-7}	1×10^{-8}
Sulphide	Orion	1.1	1.3	1.2	1.2	1.5	1.6
	Beckman	1.2	1.3	1.3	1.3	1.4	1.6
	Corning	1.2	1.2	1.3	1.3	1.6	1.6
Silver	Orion	1.2	1.2	1.3	1.4	1.5	
	Beckman	1.2	1.3	1.3	1.5	1.6	
Chloride	Orion	1.1	1.3	1.3	1.6		
	Beckman	1.2	1.2	1.3	1.6		
Iodide	Orion	1.2	1.2	1.2	1.3	1.4	1.7
	Beckman	1.2	1.4	1.3	1.3	1.5	1.7
Mercury	Orion	1.2	1.3	1.3	1.3	1.4	1.6
Bromide	Orion	1.2	1.3	1.5	1.8	1.8	
	Beckman	1.3	1.4	1.4	1.7	1.8	
Cyanide	Orion	1.2	1.2	1.4	1.5		
Fluoride	Orion	0.2	0.2	0.3	0.5		
	Beckman	0.2	0.2	0.2	0.5		
	Corning	0.2	0.2	0.3	0.4		
Cupric	Orion	0.8	0.8	0.9	1.0	1.5	1.7
	Corning	0.9	0.9	1.0	1.0	1.4	1.6
Lead	Orion	0.5	0.6	0.7	1.2		
Cadmium	Orion	0.5	0.5	0.5	0.6	1.3	
Sodium	Orion	0.4	0.8	1.0			
	Corning	0.5	0.8	1.1			
Calcium	Orion	0.2	0.2	0.4			
	Corning	0.3	0.3	0.4			
Divalent Cations	Orion	0.2	0.2	0.4			
	Corning	0.3	0.3	0.4			
Potassium	Orion	0.2	0.2	0.5	0.6		
	Corning	0.3	0.2	0.6	0.6		
Fluoroborate	Orion	0.4	0.5	0.7			
Perchlorate	Orion	0.2	0.2	0.4			
Nitrate	Orion	0.2	0.3	0.6			
	Corning	0.3	0.3	0.6			
Chloride (liquid exchanger)	Orion	0.2	0.2	0.4			
	Corning	0.3	0.3	0.5			

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