ION-SELECTIVE SENSORS

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ABSTRACT

The authors survey the operating principles, the selectivity and analytical applications of ion-selective electrochemical sensors. Several potentiometric and titration methods for various ion determinations are described.

INTRODUCTION

In the last decade, ion-selective electrodes have aroused a great deal of interest from both theoretical and practical points of view and their role in analytical chemistry has been steadily increasing.

If we speak about ion-selective electrodes, it is important to define this concept. We call ion-selective electrodes those electrochemical sensors which give rise to a reversible electrode potential for an individual ionic species in a given activity range, which is influenced by other ionic species only under given conditions. Accordingly the concept of ion-selectivity is strictly related to the minimum concentration ratio of the other ion to the reversible ionic species, which still does not disturb the determination of the appropriate component.

It is important to emphasize this condition, because one can often observe misunderstandings in the interpretation of ion-selective electrodes both in conference discussions and in the literature. That is to say, by interpreting the 'ion-selectivity' concept without the restrictions mentioned, people could easily expect 'wonders' from this kind of electrode, which the electrode cannot produce. However, the concept of ion-selective electrodes must be narrowed down even within the definition mentioned. That is to say, according to the given definition, 'ion-selectivity' is shown by many types of electrodes, e.g. metal electrodes, electrodes of the second kind and so on.

Table 1. Ion-selective electrodes

1. Glass electrodes	2. Liquid membrane electrodes
(a) pH	(a) charged matrix
p(cation)	(b) uncharged matrix
(b) enzyme	(c) extraction type
3. Precipitate based electrodes	
(a) on the basis of preparation	(b) on the basis of the application
homogeneous	cation selective
heterogeneous	anion selective

However, the group of ion-selective electrodes comprises only those electrodes at the surface of which electrode reactions are taking place without electron transfer, that is, the electrode response is based only on ion-exchange reactions.

The ion-selective electrodes can be divided into many subgroups (*Table 1*).

The development of ion-selective electrodes covers several periods. The first step was the discovery of the pH glass electrode at the beginning of this century by Cremer[1]. Later on Lengyel and Blum[2] observed the alkali-ion sensitivity of the glass electrodes. The field of glass electrodes was further developed by Nikolsky, Eisenman and Schwabe and others, as well as by Csákvàry and co-workers[3-8].

Guilbault and Montalvo[9] made further use of the alkali-ion sensitive glass electrode. They coated the surface of the glass electrode with an appropriate enzyme, e.g. with urease or 1-aminoacid oxydase, which was incorporated in polyacrylamide. These electrodes are sensitive to nitrogen-containing organic compounds, e.g. urea or amino acids. The electrodes work in the following way: the enzyme decomposes the organic compound and the glass electrodes respond to the ammonium ion formed.

In the field of ion-exchange electrodes Gregor, Lakshminarayanaiah, Eisenman and other scientists[10-12] have carried out fundamental investigations and towards the middle of the 'sixties, liquid ion-exchanger-based electrodes were developed which were primarily selective to alkaline earth metal ions, but to other ions also to some extent.

Simon and co-workers[13] have developed an antibiotic-based potassium ion-selective electrode. A further kind of electrode is the so-called extraction type electrode, developed by Coetzee and Freiser[14], in which the extraction medium dissolved in an indifferent solvent can bind on to the electrode surface certain ion-species in a selective way.

Experiments for developing precipitate-based electrodes started in the 'fifties, although not in the best way. Selection of the precipitates could not be done on a theoretical basis and as our present knowledge proves, the precipitates used were such that no appropriate ion-exchange reactions could take place on their surfaces.

Tendeloo and Krups, Cloos and Fripiat, Fischer and Babcock[15-17] reported on the precipitate-based electrodes in several papers, but the potentials which they measured were only diffusion ones.

We have been working in the field of ion-selective electrodes since 1959: our work was connected to a series of earlier investigations in the course of which we had examined the behaviour of the silver iodide precipitate from a colloid chemical and many other points of view. That is why we have prepared our first electrode from silver iodide. This kind of electrode showed great selectivity towards iodide in the presence of other ions. This investigation was the first of a series as a result of which different kinds of precipitate-based electrodes have become available.

PRECIPITATE-BASED ELECTRODES

Here, we deal first of all with the theoretical discussion of precipitate-based electrodes. The phenomena will be discussed first from a thermo-

dynamic point of view and then the transient phenomena will be dealt with.

Some papers on precipitate-based ion-selective membrane electrodes—principally in the American literature—discuss the electrochemical behaviour of heterogeneous and solid-state membrane electrodes separately. However. this differentiation is disturbing, because they differ from each other only in mechanical and not in electrochemical respects. so we will treat them together.

For the theoretical interpretation of the behaviour of precipitate-based ion-selective electrodes. silver halide-based membrane electrodes were chosen. As far as precipitate-based membrane electrodes are concerned. the particle size. the defect structure of the precipitate and the adsorption phenomena on its surface are of great importance. The behaviour of the electrodes is explained on the basis of a precipitate ion-exchange reaction.

The thermodynamic approach for the interpretation of the electrode phenomena is carried out through the establishment of the electrochemical potentials. If the electrode is placed in a solution containing the reversible ion. the condition of the equilibrium is such that both the electrochemical potentials of the ion present in the solution and the ion present in the membrane phase should be the same.

The membrane potential can be derived as follows:

$$\overset{*}{\mu}_s = \mu_s + z_i F \psi_s$$

$$\overset{*}{\mu}_m = \mu_m + z_i F \psi_m$$

$$E = E^0 + (RT/z_i F) \ln \{(a_i)_s/(a_i)_m\}$$

The electrode standard potential is obtained from the chemical standard potentials. The examination of the standard potential value is a very important
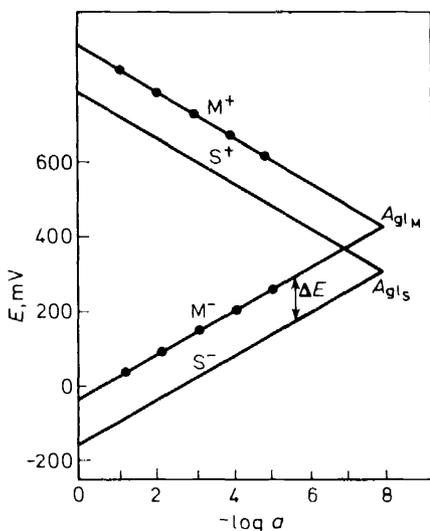

Figure 1. Comparison between the potentials of a silver iodide-based membrane electrode (M) and that of the corresponding electrode of the second kind (S).

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question in relation to the behaviour of the electrodes. With the silver halide type electrodes the question may arise, what is the relation between the standard potential of the electrode and the standard potential value of the corresponding electrode of the second kind. This problem was studied in detail by Marton. In *Figure 1* we can see that there are differences between the potential values of the membrane electrode and the electrode of the second kind, and, accordingly, between their standard potential values, too. Furthermore, it was also found that by changing the exposure time of the precipitate built into the membrane, the difference mentioned will also change. From this, it can be concluded that the fundamental difference between a membrane electrode and an electrode of the second kind is that for an electrode of the second kind, not only the dehydration of the hydrated ions on the electrode surface plays a role in the establishment of the electrode potential, but the electron transfer reaction does also. Due to this difference, some practical and theoretical consequences should be mentioned. It was found by experiment that by exposing an electrode of the second kind to light, its potential changes. Similarly, redox components will also cause a change in its potential value. However, membrane electrodes, the sensing part of which is a suitably prepared precipitate in a supporting material, e.g. in silicone rubber, are only slightly or not at all sensitive to the reactions mentioned.

A further difference between the two kinds of electrodes is that the temperature dependence of the standard potentials differs from one to the other not only in actual potential values, but also in sign (*Figure 2*).
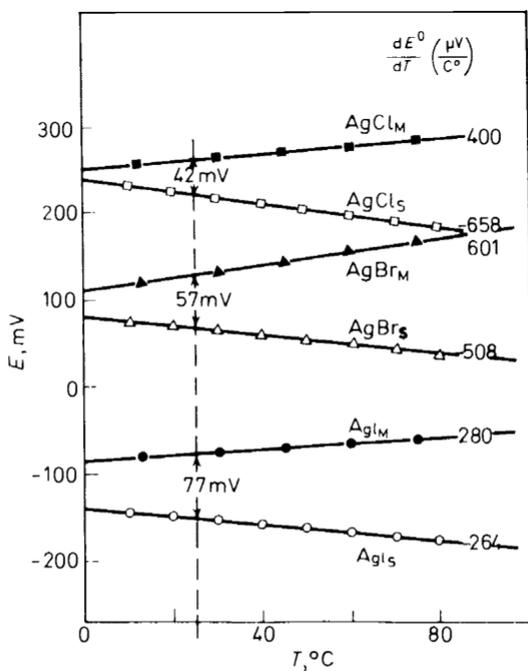

Figure 2. Dependence of the standard potential of halide-selective membrane electrodes (M) and of electrodes of the second kind (S) on temperature.

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In a solution containing not only the ion to which the electrode is reversible but another ion too, which also forms a precipitate with one of the components of the membrane matrix, the following precipitate exchange reaction is established:

$$AgI + K \rightleftharpoons AgK + I$$
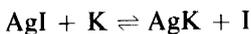
$$K_{ik} = (/a_i/_s/a_k/_m/)(/a_k/_s/a_i/_m)$$

On the basis of this exchange equilibrium the following equation can be derived for the potential of the membrane electrode by substituting this value into the potential equation

$$E = E_0 + \frac{RT}{z_iF} \ln (a_i)_s \sum_n K_{ik} \frac{(a_k)_s}{(a_i)_s}$$

$$= E_0 + \frac{RT}{z_iF} \ln (c_i)_s \sum_n K_{ik} \frac{(c_k)_s}{(c_i)_s} \times f_\pm$$

where a_i, c_i and a_k, c_k are the activities and concentrations. n is the number of ions taking part in the exchange reaction. $f_\pm$ is the mean activity coefficient. and K_{ik} is the selectivity constant of the electrode.

The selectivity constant can also be deduced from the exchange equilibrium and has the general form

$$K_{ik} = \frac{S_{ji}^{1/a}}{S_{jk}^{1/w}} = \frac{(a_i)_s^{b/a}}{(a_k)_s^{v/w}}$$

where $(a_i)_s$ and $(a_k)_s$ are the equilibrium activities of the ions taking part in
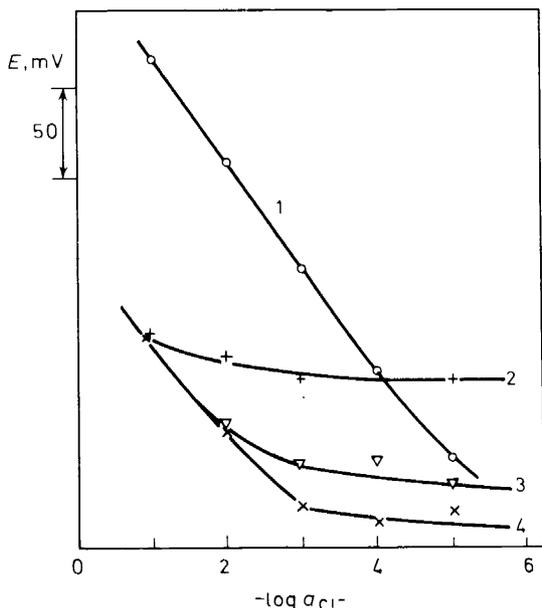

Figure 3. Selectivity of Br membrane electrode to Br in Br⁻–Cl⁻ binary mixtures: 1 calibration curve for Br⁻ electrode; 2 10^{-4}M KBr in Cl⁻ solution; 3 10^{-5}M KBr in Cl⁻ solution; 4 10^{-6} M KBr in Cl⁻ solution.

the precipitate exchange reaction which is measured when co-precipitation starts; a, b, v, w are the stoichiometric constants of the precipitates. $(I_j)_a - (I_i)_b$, and $(I_j)_w - (I_k)_v$, are both built-in in the membrane or formed during the exchange reaction, and S_{ji}, S_{jk} are the appropriate solubility products.

When univalent ions form the precipitates, then the equation can be reduced to the following expression

$$K_{ik} = S_{ji}/S_{jk}$$

The validity of the previous equation has been proved experimentally with various ion-selective electrodes.

The determination of the selectivity constant can be carried out directly or indirectly. It must be emphasized that the solution tested should contain both the appropriate ion and other ions when either the direct or indirect method for the determination of the selectivity constant is used. The activity of the appropriate ion is constant and relatively low, while that of the interfering ion varies when the direct method is used. The opposite is found with the indirect method (*Figures 3* and *4*).
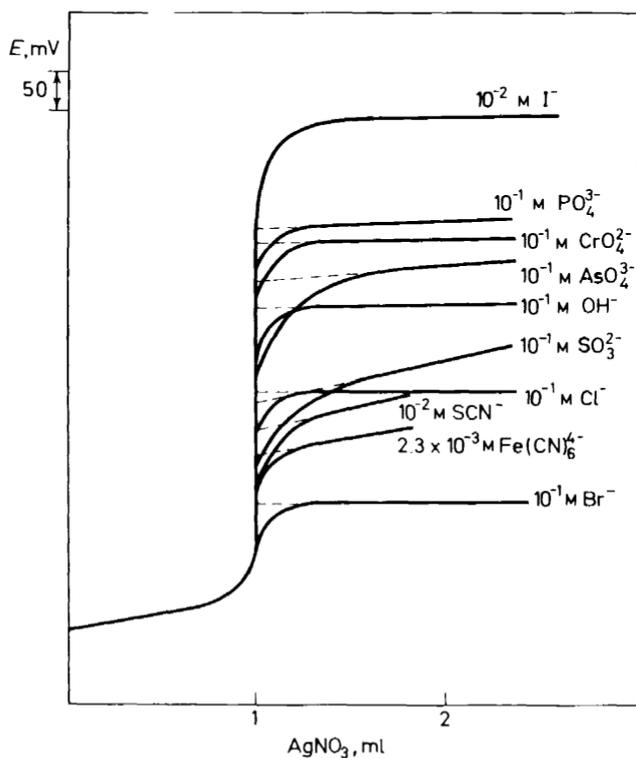
*Figure 4.* Investigation of selectivity of I⁻ membrane electrode to various anions by potentiometric titration.

If the selectivity constant is not smaller than 10^{-6}, it is advisable to use the direct method for the determination. However, if the selectivity constant is smaller than the value mentioned, then the direct method cannot be used and it is advisable to use the indirect method instead.

Table 2. Selectivity constants of halide-selective electrodes.
K_{ik}^* denotes values measured by direct method; K_{ik}^{**} denotes values measured by indirect method.

Ion	Chloride-selective electrode			Bromide-selective electrode			Iodide-selective electrode		
	K_{ik} calc.	K_{ik}^* meas.	K_{ik}^{**} meas.	K_{ik} calc.	K_{ik}^* meas.	K_{ik}^{**} meas.	K_{ik} calc.	K_{ik}^* meas.	K_{ik}^{**} meas.
Cl^-	1	1		2.0×10^{-3}	1.8×10^{-3}	6.0×10^{-3}	9.6×10^{-7}	2.1×10^{-4}	3.7×10^{-7}
Br^-				1	1		2.0×10^{-4}		1.8×10^{-4}
SCN^-				1.5×10^{0}	0.2×10^{0}		3.0×10^{-4}		2.4×10^{-4}
OH^-							1.0×10^{-8}		0.9×10^{-8}
CrO_4^{2-}	5.2×10^{-5}		4.5×10^{-5}	2.5×10^{-7}		1.1×10^{-7}	5.0×10^{-11}		6.6×10^{-11}
CO_3^{2-}	6.3×10^{-5}		4.6×10^{-5}	3.1×10^{-7}		1.0×10^{-7}			
PO_4^{3-}	1.3×10^{-4}		0.5×10^{-4}	6.3×10^{-7}		3.1×10^{-7}	1.2×10^{-10}		0.2×10^{-10}
AsO_4^{3-}	3.3×10^{-4}		2.0×10^{-4}	1.6×10^{-6}		1.2×10^{-6}	3.2×10^{-10}		2.6×10^{-10}
$(CN)_6^{4-}$							2.4×10^{-6}		3.5×10^{-6}
I^-							1	1	

Table 2 presents results for the selectivity constants calculated and measured.

PRESENCE OF COMPLEXING AGENTS

A further interesting problem is to study the behaviour of halide-selective electrodes in the presence of complexing agents. It was found experimentally that all silver halide membrane electrodes responded to complexing agents such as cyanide or thiosulphate in solutions containing both the appropriate halide ion and the complexing agent. Further, it was also found that the response of the halide-selective electrodes to a complexing agent started when the activity reached that of the appropriate halide ion. All cyanide measurements were carried out in solutions of pH higher than 11. because the electrode measures only the cyanide ion activity and the dissociation constant of the hydrogen cyanide is higher than 10^{-9}.

All halide electrodes. however. showed the same selectivity to various anions in the presence of cyanide as in the presence of the appropriate halide ion. *Table 3* shows this comparison for a silver iodide-based cyanide electrode.

Table 3. Selectivity constants of a silver iodide-based membrane electrode to various anions.

Ion	Selectivity constants in the presence of	
	CN^-	I^-
Cl^-	10^{-5} to 10^{-6}	10^{-6}
Br^-	10^{-3} to 10^{-4}	10^{-4}
I^-	1	
CN		1
NH_4^+	10^{-5} to 10^{-6}	10^{-6}
SO_4^{2-}	10^{-5} to 10^{-6}	10^{-6}

The theoretical understanding of the behaviour of ion-selective electrodes in the presence of complexing agents is far from complete. so only the theoretical aspects which have been proved experimentally are summarized. The interpretation is based on the dissolution of silver halide salts by complexing agents. The potential established on the surface of the cyanide membrane electrode is the result of the continuous dissolution of the silver halide precipitate and therefore the exhaustion of the electrode in time is understandable. However. as this interpretation does not answer the selectivity problem of the electrodes mentioned previously, it seems useful to discuss the behaviour of the halide electrodes in the presence of complexing agents on the basis of exchange reaction mentioned in the case of precipitate-forming ions. In this discussion, diffusion phenomena are neglected and the following interpretation. given for the behaviour of the electrodes responding to complexing agents. can be considered as a zero-order approximation :

The basic reaction and the potential equation are as follows:

$$AgX + 2CN^- \rightleftharpoons Ag(CN)_2^- + X^-$$
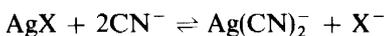
$$E = E_0 + \frac{RT}{zF} \ln (a_I + K_{CN,I}a_{CN}^2)$$

The validity of this equation was proved experimentally in the range of 10^{-4} to $2M$ cyanide concentration. All solutions were made $2M$ with respect to sodium hydroxide. The results are summarized in *Figure 5*. where the theoretical curve is calculated according to the above equation.
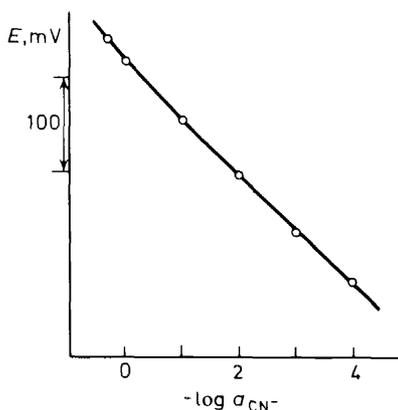

Figure 5. Calibration curve for determination of cyanide, using silver iodide-based electrode versus SCE.———calculated curve; o measured point.

The equations presented earlier have been deduced and interpreted on a thermodynamic basis. Equations deduced thermodynamically can only describe the states established after equilibrium has been reached. However, kinetic investigations generally give further useful information about the behaviour of electrodes.

We would like to emphasize that if the rate of the electrode reactions is not sufficiently high, then the reversibility of the electrode to an ionic species in question will decrease. To examine the rate of the exchange reactions is very important, because it can serve as a basis for selecting electrode materials. Furthermore, the study of the kinetic behaviour and the transient phenomena of the electrodes is very important from a practical point of view also. especially if they are used in controlling systems as sensors.

Recently studies have been made on the transient phenomena of ion-selective electrodes other than glass electrodes and results have been published. Unfortunately, research on this subject has not been carried out under the best conditions as the instruments generally used for the measurement of the e.m.f. versus time curve had a relatively high time constant, so the data

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determined cannot be used for kinetic studies. The results can also be misleading because instead of the response time of the electrode, that of the measuring cell, involving one or more liquid junction potentials, was measured. The liquid junction potentials are also time-dependent, so they may upset the evaluation of the results.

The transient phenomena can be measured in two different ways: by the immersion method, in which the electrode is immersed in the solution at $t = 0$ time instant, and the injection method, in which a solution of given concentration is injected into the following system with constant speed. A variation of the former method was carried out in our Institute, and it was found that two different concentrations of the appropriate ion had interchanged round the electrode within one millisecond, and the change in the electrode potential was recorded with an oscilloscope. The results were as follows: the e.m.f. versus time reached a constant value within a few hundred milliseconds in the case of the iodide electrode and the transient phenomena of the electrode can be described with one exponential equation; the response time of the electrode is independent of the thickness of the membrane layer and depends on the concentration level of the appropriate ion and on the concentration jump only to a small extent; it also depends on the direction of the concentration jump; a great excess of other ions generally decreases the electrode response time; the response time of the cyanide electrode is the same as that of a halide electrode, which also shows that the mechanism of the response of a halide-based electrode to a complexing agent is the same as that of the electrode to precipitate-forming ions.

In the recent literature other types of units for the investigation of transient phenomena can also be found[18–19].

ELECTRODES OTHER THAN GLASS

The theory of glass electrodes was elaborated by Nikolsky[4, 5]. Later the theoretical description of these electrodes was modified and further developed by Eisenman. The equation for the potential, valid for glass electrodes, can be expressed

$$E = E^0 + (RT/F) \ln (a_H^{1/n} + K^{1/n} a_B^{1/n})^n$$

Eisenman and co-workers[12] also studied other ion exchangers and found that the behaviour of the solid ion-exchangers and that of the liquid ion-exchangers can be treated on the same principle. The solid ion-exchangers as well as liquid ion-exchangers, which consist of completely dissociated salts, may be uniformly described with the same equation. For solid ion exchanger and completely dissociated liquid ion exchanger

$$E = \frac{RT}{F} \ln \frac{a'_1 + \left[\left(\frac{S_2}{S_1}\right)^2 \frac{\lambda_2}{\lambda_1}\right] \times a'_2}{a''_1 + \left[\left(\frac{S_2}{S_1}\right)^2 \frac{\lambda_2}{\lambda_1}\right] \times a''_2}$$

where a_1 and a_2 are the activities of two ionic species: S_1 and S_2 are the two distribution coefficients of the ions a_1 and a_2 between water and the pure

solvent; λ_1 and λ_2 are the single ionic conductances, and $'$ and $''$ denote the solutions on the two sides of the membrane.

In the equation the equilibrium constant of the ion-exchange will be corrected by the mobilities. i.e. by the quotient of the mobilities of the ion to be measured and of that of the counter ion, through which the selectivity constant for the ion in question will be obtained. The correlation is far more complicated if we work with well associating liquid ion-exchangers. The following is valid for liquid ion-exchangers with strong association

$$E = \frac{RT}{F} \tau \ln \frac{a_1' + \left(\frac{U_{2S}}{U_{1S}} K_{12}\right) a_2'}{a_1'' + \left(\frac{U_{2S}}{U_{1S}} K_{12}\right) a_2''} + (1 - \tau) \ln \frac{a_1' + \left[\left(\frac{S_2}{S_1}\right)^2 \frac{\lambda_2}{\lambda_1}\right] a_2'}{a_1'' + \left[\left(\frac{S_2}{S_1}\right)^2 \frac{\lambda_2}{\lambda_1}\right] a_2''}$$

where U_{1S} and U_{2S} are the mobilities of the undissociated ion pairs, K_{12} is the equilibrium constant of the ion exchange reaction of the two species, λ is the limiting equivalent conductance of the ion exchanger recombined with the appropriate ion and τ has a transference number meaning its value is between 0 and 1.

It shows that not only the ion-exchange equilibrium. but also the conductivity of the ion-pairs forming through the membrane phase. play a role in the behaviour of the electrode.

The theory can be extended and it is valid not only for the charged and neutral ionites such as the electrodes of Simon but also for the extraction electrodes devised by Freiser. In connection with ionite electrodes it is. however. to be mentioned that they change their selectivity constants with time. in contrast to precipitate-based electrodes. The cause of this change can be explained theoretically. since the ionites—either solid or liquid—will become contaminated from the solution they are contacting.

After giving this summary on ion-selective sensors. we would like to go on to discuss the application of ion-selective electrodes.

APPLICATION OF ION-SELECTIVE SENSORS

Ion-selective sensors can be used advantageously for the determination of an individual ionic species by both direct and indirect potentiometric methods. The evaluation of the results is carried out in the former case with the help of a calibration curve prepared by using standard solutions. while it is done on the basis of the potentiometric titration curve in the latter case. Ion-selective electrodes can also be employed for measuring ion-activities in flowing systems and. furthermore. they can be applied in controlling systems as sensors.

Among the applications of ion-selective electrodes. we would like to mention only a few examples, which we think you will find most interesting.

The iodide ion-selective electrode was used successfully to determine the iodide content of mineral waters, the amount of chloride in blood and urine and, furthermore, to measure the halide content in some pharmaceutical preparations. The application of a chloride ion-selective electrode to the measurement of chloride in blood has the advantage over other methods that it was not necessary to separate the proteins before measurement. In the

course of the examination of pharmaceutical preparations we have studied organic compounds which contained the halogen in dissociated (e.g. Promethazine HCl) and in undissociated (e.g. Chlorpromazine) form. For the determinations both the direct and indirect methods have been employed.

It must be emphasized that the ion-selective electrodes sense the activity of ions, so the results obtained with the direct potentiometric method can only be converted into concentrations if mean activity coefficients of the sample solutions are known. When we applied the direct potentiometric method for the examination of organic compounds which contained halide ions, we have found that the large organic molecules seriously affected the mean activity coefficient of the sample solution. So in this case it was necessary to measure the mean activity coefficients to obtain correct results. However, if the halide is covalently bound to the skeleton of the molecule then it can only be determined after decomposition (digestion or combustion). In our work the halide was liberated after combustion by using the modified Schöniger method. The measurement of the halide ions was carried out with both direct and indirect methods. In the direct method the effect of the activity coefficient was overcome by using standard solutions, the ionic strength of which was the same as that of the sample solution. By means of the direct method, an accuracy of ± 0.05 pX could be achieved. Naturally the accuracy of the direct method is smaller if the activity of the ion measured is near the detection limit of the ion-selective electrode employed.

It is known that ion-selective electrodes are excellent indicator electrodes. We have used the indirect method also for measuring the halide content of samples obtained after combustion. The results are collected and shown in *Table 4*.

Table 4.

Compound	Sample taken mg	Halide content, %		%
		Calc.	Found	
2.6-Dinitro-chlorobenzene	18.105	17.21	17.43	+ 1.2
	24.084	17.21	17.42	+ 1.2
	21.074	17.21	17.67	+ 2.6
	24.018	17.21	17.71	+ 2.9
	20.757	17.21	17.42	+ 1.2
Chlorpromazine HCl	20.203	19.96	20.44	+ 2.4
	20.787	19.96	20.03	+ 0.3
	17.290	19.96	19.98	+ 0.1
	19.950	19.96	19.99	+ 0.1
	17.782	19.96	20.03	+ 0.3

The determination of sulphide using a sulphide-selective electrode is always carried out at pH higher than 13.0, because of the second dissociation constant of H_2S. Among various applications of the sulphide ion-selective electrode only one is discussed in detail. We have found that the hydrolysis of organic compounds can also give a way for the analysis of organic compounds. As an example a thio-compound, thiourea, is shown which slightly

hydrolyses in aqueous solution. The degree of hydrolysis of the molecule is greater than zero which was proved by potentiometric measurements using a sulphide-selective electrode in aqueous thiourea solutions. The approximate concentration of sulphide ion in alkaline 10^{-1}M thiourea solutions is extremely small—about 10^{-15}M (calculated from the Nernst equation). By adding silver nitrate (by titrating the solution with silver nitrate) in the presence of 0.1 N sodium hydroxide, the following reaction takes place:

$$H_2N-\underset{\underset{S}{\overset{\|}{}}}{C}-NH_2 + 2AgNO_3 \rightleftharpoons H_2N-C\equiv N + Ag_2S + 2HNO_3$$

$$H_2N-C\equiv N + 2AgNO_3 \rightleftharpoons Ag_2N-C\equiv N + 2HNO_3$$
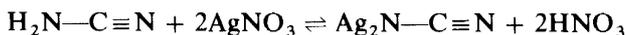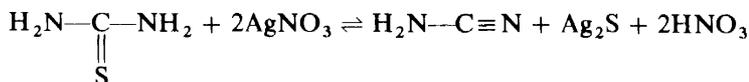
In the first step, one sulphur atom splits off to form silver sulphide and at the same time cyanamide is formed. The resulting cyanamide reacts with two more moles of silver nitrate and gives a silver cyanamide precipitate. The products of the titration were separated by filtration and were analysed gravimetrically and also for their elemental composition. Besides this, their infra-red spectra were also taken. For comparison the spectra of pure cyanamide and thiourea were also recorded. These experiments proved the reaction path shown previously. The titration allows an accurate determination of thiourea which was worked out together with our co-worker Mrs
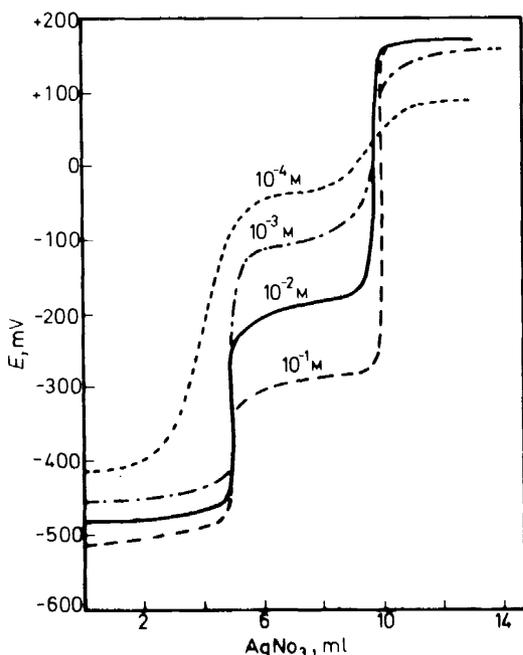

Figure 6. Potentiometric titration of 10^{-1} to 10^{-4}M thiourea solutions with standard silver nitrate solution, in 1M sodium hydroxide.

Kucsera. The reaction, which takes place rapidly in the course of the titration is followed conveniently by a sulphide ion-selective electrode in 10^{-1} to 10^{-3}M thiourea solutions. In 10^{-4}M concentrations the titration requires longer. The titration curve is shown in *Figure 6*.

Both potential jumps can equally be used for the calculation of the amount of thiourea. For the first equivalence point the equivalent weight of thiourea is one half, in the second one fourth of the molecular weight.

For comparison, the curves of three potentiometric titrations are presented (*Figure 7*): curve 1 was obtained for the titration of cyanamide alone, curve 2, for thiourea alone, whereas curve 3 is appropriate when both compounds
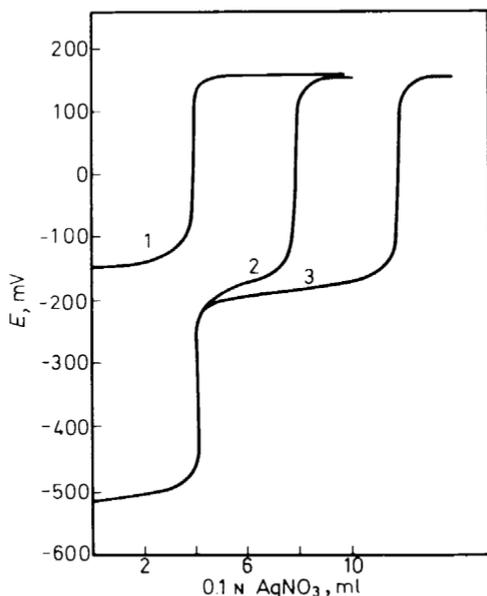

Figure 7. Titration of cyanamide (1), thiourea (2) and cyanamide plus thiourea (3) with silver nitrate solution in 1M sodium hydroxide.

were present in the solution to be titrated. The consumption of titrant at the second step of titration curve 3 has increased by the amount of titrant equivalent to that of cyanamide present.

The silver iodide-based ion-selective electrode can be used for measuring cyanide, e.g. in waste water. The determination of cyanide has to be carried out in solutions of pH higher than 11.0 at which the dissociation of HCN is complete. The cyanide electrode was employed for measuring CN^- activities continuously in sewage and as a sensor in the elimination of CN^- with OCl^-.

In this lecture the behaviour and some examples of the application of ion-selective electrodes have been shown. Further research along these lines is in progress.

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