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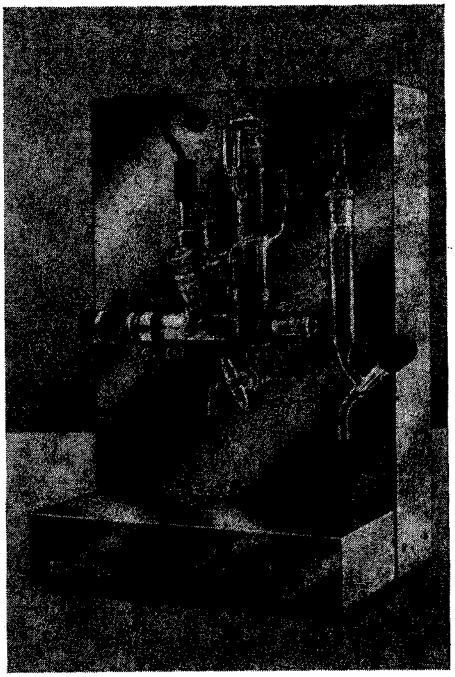

Cellule à circulation forcée du Professeur Schwing pour électrochimie

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Cette cellule à circulation forcée a été réalisée dans les laboratoires de chimie-physique et d'électroanalyse de l'Institut de Strasbourg par une équipe de recherche associée au CNRS. De conception modulaire, elle permet la mise en oeuvre de la quasi totalité des méthodes électroanalytiques et spectrotitrimétriques et en particulier elle remplace avantageusement les montages utilisant des électrodes à goutte de mercure, à fil ou disque tournant ou à fil vibrant.

Elle comporte comme élément essentiel une petite pompe centrifuge entraînée par un moteur à vitesse constante tournant à près de 3000 tours/minute; dans ces conditions la solution parcourt très rapidement le circuit fermé constituant le volume intérieur de la cellule. Quatre rodages normalisés permettent l'introduction de diverses électrodes ou accessoires dans le courant liquide. Un cylindre rodé sert à la fois de plongeur à circulation de fluide pour thermostater et de dispositif pour éliminer l'air restant au-dessus de la solution étudiée.

Un tel montage conduit à une très grande reproductibilité des courbes voltampérométriques des systèmes électrochimiques mis en oeuvre, courbes nécessaires à la mise au point des titrages, qui peuvent s'effectuer dans la cellule même, soit par injection de réactif titré à l'aide d'une burette à piston, soit par coulométrie; la détection est réalisée soit par potentiométrie classique, par ampèrométrie ou dead-stop, soit par spectrophotométrie la cellule grace à son procédé de pompage permettant d'alimenter la cuve à circulation d'un spectrophotométre. La spectrotitrimétrie sera particulièrement utile lorsque la détection électrochimique conduit à une modification de l'état de surface des électrodes indicatrices.

A. M. Gary, M. Rognette et J. P. Schwing. Bull. Soc. Chim. Octobre 1971 page 3779
A. M. Gary et J. P. Schwing. Bull. Soc. Chim. Octobre 1971 page 3786
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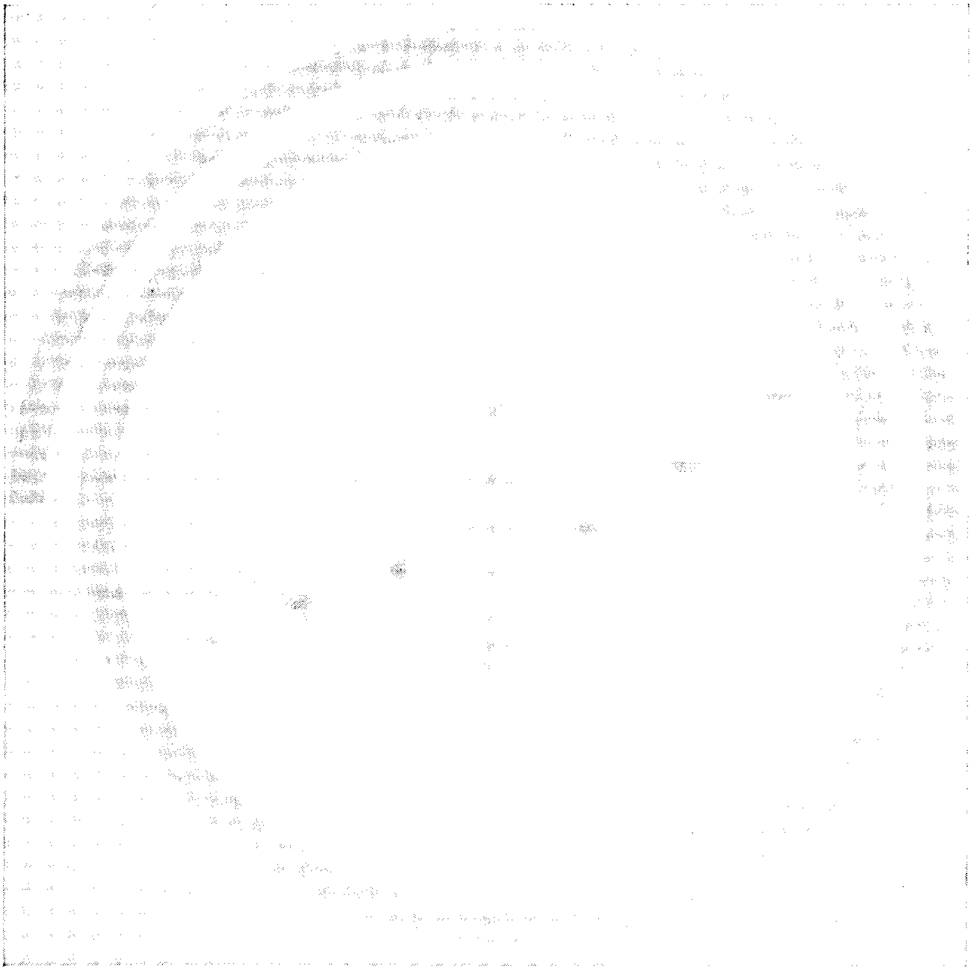

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REVIEW

THEORY AND APPLICATIONS OF ION-SELECTIVE ELECTRODES

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(Received 1st June 1972)

CONTENTS

In the mid 19th century, physiologists began to notice the electric currents and the differences between electrical potentials which are formed between intact and damaged places in various parts of organisms. As early as 1848, Du Bois-Reymond[144,619] proposed that the surface of biological formations with properties similar to an electrode of a galvanic cell is the source of these bioelectrical phenomena. The properties of biological membranes could not, however, be established in greater detail until the basic physical chemistry of at least simple models had been established. Thermodynamic relations for equilibria on membranes were formulated by Gibbs in 1875[203]. At that time, there was, of course, no theory of electrolyte solutions (Arrhenius, 1887) so that Gibbs' work does not mention ions and electric potentials.

A vital step in this field is represented by Nernst's[426,427] and Planck's[507,508] papers on transport processes in electrolytes. In these papers, the concepts of the diffusion potential, which is formed in the case of unequal diffusion rates of electrically charged components of the electrolyte, and of the *electric potential on the liquid–liquid interface* that follows from these different rates, were defined. The actual electrochemistry of membranes was founded in 1890 by Wilhelm Ostwald[467] who considered the *semipermeable membrane*, which is impermeable for a certain kind of ion. The electric potential difference on such a membrane is a limiting case of the potential difference on the liquid–liquid interface when the mobility of one kind of ion approaches zero. A small number of non-permeating ions still penetrates through the interface and forms there an electric double-layer which is the source of the electric potential difference. Ostwald writes that "not only currents in muscles and nerves but also the mysterious phenomena of electric fish will after all be explained by the properties of semipermeable membranes". A membrane theory of the electric properties of cells and tissues was first given by Bernstein[48] in 1902. This theory is the basis of the present-day concept of bioelectric potentials.

The turn of the 19th to the 20th century brought an intensive search for suitable models for membrane systems. These models fall into two groups, *compact or liquid* ("oil") *membranes*[51,52,237,362,428] and *porous membranes*[50]. During the study of compact membranes, the glass electrode was discovered[121,238]. This membrane exhibits a pronounced selectivity for a certain kind of ion, in this case, hydrogen ions.

However, in the 1920s and 1930s, models for biological membranes were sought among the porous membranes; the work of Michaelis (*e.g.* ref. 395) and Sollner (for a summary see ref. 619) was of particular importance in this field. In fact, it was on porous membranes that the relations for the Donnan membrane potentials[142] were verified. The theory of the membrane potential of porous membranes, which are easily permeable for some kinds of ion with a certain charge but poorly permeable for ions with the opposite charge, was developed by Teorell[643], and by Meyer and Sievers[392]. The theory, however, can also be used for compact membranes.

In 1935, Danielli and Davson[130] proposed a theory for the membranes of cells and cell organelles, which are presumed to have the nature of very thin compact liquid membranes (composed of a bimolecular layer of phospholipids, covered on both sides by a single protein layer). To explain the properties of the membrane potential, at different permeabilities of such a membrane towards sodium and potassium ions, Goldman[206], and Hodgkin and Huxley[275], worked out a theory of membrane potentials for such cases. Very thin artificial "black" phospholipid membranes were first obtained by Mueller *et al.*[414].

Meanwhile, it became obvious that the theory of the glass electrode, based on the concept of the concentration cell or the Donnan potential with diffusible hydrogen ions, cannot explain certain properties of this electrode, predominantly its pronounced selectivity towards sodium ions, which appears with glasses of a certain composition[344]. This led Nikolsky and Tolmacheva[436] to the ion-exchanger concept of the glass membrane. Finally, a theory of the glass electrode, analogous to the Goldman–Hodgkin–Huxley theory of the bioelectric potential, was proposed by the physiologist, Eisenman, and his co-workers[165].

Liquid membranes containing a dissolved ion exchanger were first used by Sollner and Shean[621,622]. Their membrane was generally selective for all cations, rather than for a certain kind of cation. In 1961, the first ion-selective electrodes with precipitate-containing heterogeneous membranes were prepared by Pungor and Hallós-Rokosinyi[522]. Compact ion-exchange membranes from single crystal materials were obtained by Frant and Ross[189]

During research on several antibiotics which slow down oxidative phosphorylation in mitochondria[341], it was found that, in the presence of alkali metal ions, they also give rise to specific electric potentials on artificial membranes[414]. This fact led, on one hand, to the development of ion-selective electrodes for ions of some alkali metals[627] and, on the other hand, to an understanding of ion transport through biological membranes in oxidative phosphorylation (see *e.g.* ref. 399). A liquid membrane with an ion exchanger of anionic type, selective for divalent cations, was discovered by Ross[561].

The field of ion-selective electrodes as well as membrane biochemistry and electrochemistry are progressing rapidly, as is shown even by literature references alone. The present review is an attempt to give a picture of the situation in the field of ion selective electrodes at the beginning of the year 1972. First, the theory of membrane potentials on membranes of different kinds is discussed, then some points common to all ion-selective electrodes are characterized, and finally the basic experimental properties of various types of electrodes, together with their analytical applications, are reviewed.

During the last few years, ion-selective electrodes have been dealt with in a number of informative articles and reviews (refs. 75, 96, 117, 145a, 288, 308, 326a, 438, 439, 518, 525, 537, 538, 540, 611). Various types of ion selective electrodes are manufactured by the firms Beckman[45,85], Coleman[104], Corning Glass Works[115], Foxboro[180-184], Orion Research[447], Philips Gloeilampenfabrieken[490,491], Radelkis Electrochemical Instruments[531], Radiometer[373,532-534], and "Monokrystaly", the Research Institute for Single Crystals, Turnov[629b]. The firm, Orion Research, publishes a regular bulletin dealing with advances in ion-selective electrodes, from the point of view of the application of their products[449-466]

THEORY OF MEMBRANE POTENTIALS

Principal concepts

An elastic two-dimensional plate is denoted in physics by the term *membrane* (*membrana* = parchment). In chemistry, the term denotes a thin body separating two liquid phases, where at least some of the components of the phases can pass through it. If the membrane is permeable to all components of the system to the same extent, its sole effect on the system lies in preventing rapid mixing of the components of the two phases. When the system is not in equilibrium, while the liquid phases themselves are in equilibrium, the presence of the membrane can hinder rapid balancing of the osmotic pressure between the two liquids. A membrane which is not equally permeable for all components is called a *semipermeable membrane.* Membranes separating two electrolyte solutions, which are not equally permeable for all kinds of ions, are the topic of the present considerations. This kind of semipermeable membrane will be called an *electrochemical membrane.* An important property of electrochemical membranes is the formation of an electric potential difference between the two solutions. This difference is called the *membrane potential* $\Delta\varphi_M$, $\varphi_2 - \varphi_1 = \Delta\varphi_M$, corresponding to the following scheme:

$$\begin{array}{c|c|c} \text{solution 1} & \text{membrane} & \text{solution 2} \\ \varphi_1 & & \varphi_2 \\ \multicolumn{1}{r}{x=p} & & \multicolumn{1}{l}{x=q} \end{array}$$

where x denotes the linear coordinate, according to which the system is ordered, and φ_1 and φ_2 are the electrical potentials of solutions 1 and 2.

It should be noted that, according to the IUPAC convention[376], in the graphical horizontal representation of a multiphase system, the electric potential of the phase on the left-hand side is subtracted from that of the phase placed to the right. The symbol φ denotes the so-called inner potential of the given phase (see *e.g.* ref. 327, p. 141).

The partial molar Gibbs (free) energy of the *i*th component of the given phase, α, is the electrochemical potential of this component, $\tilde{\mu}_i(\alpha)$, taking into account that the phase is electrically charged (see *e.g.* ref. 327, p. 141).

Generally, the chemical properties of the phase components are affected by their charge; however, this effect is perceptible only at charge values which are not encountered in current electrochemistry. In those cases dealt with in the present review, the situation can be simplified; the chemical properties of a component, characterized by its standard chemical potential, $\mu_i^0(\alpha)$, and by its activity, a_i, can be considered independently from its electric properties, characterized by its charge, z_i, and the inner potential of the phase. Then the following equation may be written for the electrochemical potential:

$$\tilde{\mu}_i(\alpha) = \mu_i^0(\alpha) + RT \ln a_i(\alpha) + z_i F\varphi(\alpha) \quad (1)$$

Let us consider two phases, α and β, *e.g.* a solution and a membrane which are in contact, both containing the *i*th component. If they are in equilibrium, then

$$\tilde{\mu}_i(\alpha) = \tilde{\mu}_i(\beta)$$
$$\mu_i^0(\alpha) + RT \ln a_i(\alpha) + z_i F\varphi(\alpha) = \mu_i^0(\beta) + RT \ln a_i(\beta) + z_i F\varphi(\beta) \quad (2)$$

When the particular phases are not in equilibrium as a whole (especially when mass transport occurs in some of them), but the system is in equilibrium at least at the interface, eqn. (2) may still be used but the values $a_i(\alpha)$, $a_i(\beta)$, $\varphi(\alpha)$, and $\varphi(\beta)$ must be related to the immediate vicinity of the interface. Such values are then denoted by symbols relating to the particular interface, *e.g.* $a_i(\alpha, p)$, $a_i(\beta, p)$, $\varphi(\alpha, p)$, and $\varphi(\beta, p)$.

In the case of a non-equilibrium state, mass transport occurs, and when charged particles are involved, there is also charge transport. The transport rate of a certain kind of component of the system is expressed by the mass flux, J_i (the amount of substance, *i.e.* "the number of moles", which passes through a unit area during unit time). The mass flux is proportional to the particle mobility, U_i, to its concentration at the given place, c_i, and to the driving force of the transport process; the particle mobility, U_i, has dimensions of kg^{-1} s mol in basic SI units; the more frequently used electric mobility, $u_i = |z_i| FU_i$, has the basic unit, $\text{m}^2\ \text{s}^{-1}\ \text{V}^{-1}$. The relationship $u_i = \lambda_i / F$, where λ_i is the equivalent ionic conductivity, is valid for u_i. Thus, $U_i = \lambda_i / |z_i| F^2$. In the case when the effect of external mechanical forces on the system is negligible (*i.e.* there is no convection), the only driving force is the electrochemical potential gradient, which arises from a transport process caused by osmotic and electric forces. Then, in the case of changes along the x-coordinate,

$$J_i = -U_i c_i \partial\tilde{\mu}_i / \partial x \quad (3)$$

When a dilute solution is used, activities can be replaced by concentrations, and thus the Nernst–Planck equation is produced:

$$J_i = -U_i RT\, \mathrm{d}c_i/\mathrm{d}x - z_i F U_i c_i\, \mathrm{d}\varphi/\mathrm{d}x \quad (4)$$

Under these conditions, we have:

$$U_i RT = D_i \quad (5)$$

where D_i is the diffusion coefficient of the *i*th component.

Membrane potentials in the absence of inner diffusion potential

If the membrane phase has the same composition throughout, the membrane potential depends on the activities of the ions in the solutions with which the membrane is in contact. Any process inside the membrane is without effect on the membrane potential. A very simple case of this kind is the solid-state membranes from silver halides (see para 1, below). Membranes which completely prevent transfer of a certain kind of ions are characterized by formation of the Donnan potential (para 2, below).

1. *Solid-state membranes*

These membranes are made of non-porous materials which are practically insoluble in the electrolyte with which they are in contact. The ions forming the electrolyte are usually different from the ion which carries the charge inside the membrane (the Ag^+ ion in the case of silver halides).

Equilibrium with one kind of ion in the electrolyte[74]. Let us consider an electrochemical membrane made from a compact solid material (non-porous), *e.g.* from a sparingly soluble salt BA, which separates two solutions with different concentrations of the anion of this salt, c_2 and c_1. Owing to the different activities of these ions, a membrane potential corresponding to the equilibrium state is formed between the two solutions. There is no mass transport within the membrane so that there is no diffusion potential. For equilibrium at both interfaces

$$\begin{aligned} \tilde{\mu}_{B^+}(1) &= \tilde{\mu}_{B^+}(p) \\ \tilde{\mu}_{A^-}(1) &= \tilde{\mu}_{A^-}(p) \end{aligned} \tag{6}$$

i.e.

$$\begin{aligned} \mu^0_{B^+}(s) + RT\ln a_{B^+}(1) + F\varphi(1) &= \mu^0_{B^+}(m) + F\varphi(m) \\ \mu^0_{A^-}(s) + RT\ln a_{A^-}(1) - F\varphi(1) &= \mu^0_{A^-}(m) - F\varphi(m) \end{aligned} \tag{7}$$

where s denotes the solution and m the membrane. After adding eqn. (7) and rearranging, we get (regarding the relation $\mu^0_{B^+}(m) + \mu^0_{A^-}(m) = \mu^0_{BA}$)

$$\mu^0_{BA} - \mu^0_{B^+}(s) - \mu^0_{A^-}(s) = RT\ln a_{B^+}(1)a_{A^-}(1) = RT\ln P_{BA} \tag{8}$$

where P_{BA} is the solubility product of the salt BA. Since similar relations hold for the other membrane interface, and since $\varphi(p) = \varphi(q)$ (there is no liquid junction potential inside the membrane) the formula for the membrane potential can be derived from eqn. (7):

$$\Delta\varphi_M = \varphi(2) - \varphi(1) = \frac{RT}{F}\ln\frac{a_{A^-}(2)}{a_{A^-}(1)} \tag{9}$$

The membrane potential has, as can be expected, the same value as the electric potential difference between solutions 2 and 1, in the case of a concentration cell with two electrodes of the second kind:

$$\begin{array}{c||c|c|c|c|c||c} \text{reference} & & & \text{metal} & & & \text{reference} \\ \text{electrode} & A^-(c_1) & BA & B & BA & A^-(c_2) & \text{electrode} \end{array}$$

Equilibrium with two kinds of ions forming insoluble salts. Let us consider the case of a silver chloride membrane, where solution 1 contains, among the ions forming insoluble salts with silver(I), only chloride, while solution 2 contains chloride and iodide. When, for the iodide ion activity, the relation

$$a_{I^-} \ll \frac{P_{AgI}}{P_{AgCl}}\, a_{Cl^-} \tag{10}$$

holds, then the presence of iodide does not affect the membrane potential. If, however,

$$a_{I^-} \gg \frac{P_{AgI}}{P_{AgCl}}\, a_{Cl^-} \tag{11}$$

then silver chloride in the surface region of the membrane is converted to silver iodide, so that the new system can be represented by the scheme

$$a_{\mathrm{Cl}^-}(1) \left| \begin{array}{l} \mathrm{AgCl} \\ \alpha \end{array} \right| \begin{array}{l} \mathrm{AgI} \\ \beta \end{array} \left| \; a_{\mathrm{Cl}^-}(2),\, a_{\mathrm{I}^-}(2) \right.$$

At equilibrium,

$$\tilde{\mu}_{\mathrm{Ag}^+}(1) = \tilde{\mu}_{\mathrm{Ag}^+}(\alpha) = \tilde{\mu}_{\mathrm{Ag}^+}(\beta) = \tilde{\mu}_{\mathrm{Ag}^+}(2) \tag{12}$$

$$\tilde{\mu}_{\mathrm{Ag}^+}(1) + \tilde{\mu}_{\mathrm{Cl}^-}(1) = \mu^0_{\mathrm{AgCl}} \tag{13}$$

$$\tilde{\mu}_{\mathrm{Ag}^+}(2) + \tilde{\mu}_{\mathrm{I}^-}(2) = \mu^0_{\mathrm{AgI}} \tag{14}$$

For the membrane potential, we get

$$\Delta\varphi_{\mathrm{M}} = \frac{1}{F}\left[(\mu^0_{\mathrm{AgCl}} - \mu_{\mathrm{Cl}^-}(1) - \mu^0_{\mathrm{Ag}^+}(1) - (\mu^0_{\mathrm{AgI}} - \mu_{\mathrm{I}^-}(2) - \mu^0_{\mathrm{Ag}^+}(2))\right] = \tag{15}$$

$$= \frac{RT}{F} \ln \frac{P_{\mathrm{AgCl}}}{P_{\mathrm{AgI}}} \frac{a_{\mathrm{I}^-}(2)}{a_{\mathrm{Cl}^-}(1)}$$

For a transition case, when neither of the two inequalities, eqns. (10) and (11), is sufficiently strongly pronounced, the electrode potential depends simultaneously on the concentrations of both ions, chloride and iodide. This dependence was derived by Buck[74], on the assumption of simultaneous adsorption of silver chloride and silver iodide on the membrane surface. Here we will content ourselves with a semi-empirical relation, which expresses the $\Delta\varphi_{\mathrm{M}}$ dependence on a_{Cl^-} and a_{I^-} with sufficient precision:

$$\Delta\varphi_{\mathrm{M}} = \frac{RT}{F} \ln \frac{a_{\mathrm{Cl}^-}(2) + (P_{\mathrm{AgCl}}/P_{\mathrm{AgI}})a_{\mathrm{I}^-}(2)}{a_{\mathrm{Cl}^-}(1)} \tag{16}$$

Equation (16) is also written in the form

$$\Delta\varphi_{\mathrm{M}} = \frac{RT}{F} \ln \frac{a_{\mathrm{Cl}^-}(2) + K^{\mathrm{Pot}}_{\mathrm{Cl}^-,\mathrm{I}^-}\, a_{\mathrm{I}^-}(2)}{a_{\mathrm{Cl}^-}(1)} \tag{17}$$

where $K^{\mathrm{Pot}}_{\mathrm{Cl}^-,\mathrm{I}^-}$ is the *selectivity constant* (coefficient, ratio) of the electrode for iodide ions with respect to chloride ions. Equation (17) can also be written in the form

$$\Delta\varphi_{\mathrm{M}} = \frac{RT}{F} \ln \frac{a_{\mathrm{I}^-}(2) + K^{\mathrm{Pot}}_{\mathrm{I}^-,\mathrm{Cl}^-}\, a_{\mathrm{Cl}^-}(2)}{K^{\mathrm{Pot}}_{\mathrm{I}^-,\mathrm{Cl}^-}\, a_{\mathrm{Cl}^-}(1)} \tag{18}$$

where $K^{\mathrm{Pot}}_{\mathrm{I}^-,\mathrm{Cl}^-} = 1/K^{\mathrm{Pot}}_{\mathrm{Cl}^-,\mathrm{I}^-}$ is the selectivity constant for chloride ions with respect to iodide ions. Equations of the type (17) and (18) are sometimes called Nikolsky equations[430].

If inequality (10), *i.e.* $a_{\mathrm{Cl}^-} \gg K^{\mathrm{Pot}}_{\mathrm{Cl}^-,\mathrm{I}^-}\, a_{\mathrm{I}^-}$, holds, then eqn. (18) becomes an equation of the type of eqn. (9), so that we can write (for 25°)

$$\frac{\mathrm{d}\Delta\varphi_{\mathrm{M}}}{\mathrm{d}\log a_{\mathrm{Cl}^-}(2)} = 2.3\,\frac{RT}{F} = 59\ \mathrm{mV} \tag{19}$$

This case is then briefly characterized by the statement that the membrane potential responds with Nernstian slope, 59 mV, to chloride ions. On the other hand, when inequality (11), $a_{\mathrm{Cl}^-} \ll K^{\mathrm{Pot}}_{\mathrm{Cl}^-,\mathrm{I}^-} a_{\mathrm{I}}$, holds, the membrane potential shows a Nernstian response towards iodide ions. An electrode which responds to a single kind of ion is called specific for this ion. An electrode which, according to conditions, responds to various ions, is called selective for these ions.

The dependence of the membrane potential of a silver chloride membrane on the chloride ion activity, in the presence of various constant concentrations of iodide ion, is shown in Fig. 1.

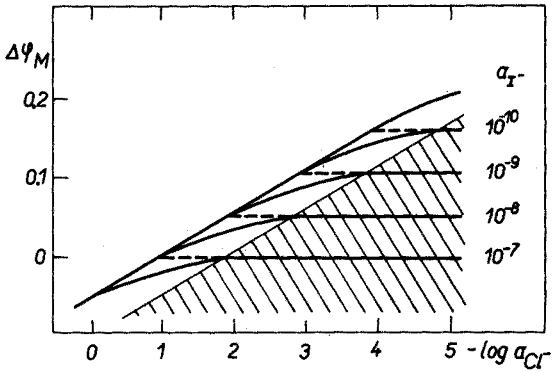


Fig. 1. The dependence of $\Delta\varphi_M$ of a silver chloride membrane on a_{Cl^-}, at a constant activity of iodide ions. The shaded area corresponds to Nernstian response to the iodide ion activity.

Membrane dissolution with formation of a complex[298,299]. Let us consider a membrane of a silver halide, AgX, which separates solution 2, containing halide ions at concentration c_x and cyanide ions in concentration c_y, from solution 1, containing halide ions in concentration c'_x. The exchange reaction takes place between the cyanide ions and the silver halide,

$$\mathrm{AgX} + 2\mathrm{Y} \rightleftharpoons \mathrm{AgY_2} + \mathrm{X}$$

with the equilibrium constant

$$K = \frac{c_{\mathrm{AgY_2}} c_{\mathrm{X}}}{c_{\mathrm{Y}}^2} = \beta_2(\mathrm{AgY_2}) P_{\mathrm{AgX}} \tag{20}$$

where $\beta_2(\mathrm{AgY_2}) = c_{\mathrm{AgY_2}}/(c_{\mathrm{Ag^+}} c_{\mathrm{Y}}^2)$. Activities in the equations have been replaced by concentrations, with the assumption that dilute solutions are involved or that the ionic strength is maintained constant by an excess of indifferent electrolyte (*e.g.* $\mathrm{KNO_3}$), so that in the latter case activity coefficients could be included in the constant β_2.

On dissolution, the X and $\mathrm{AgY_2}$ concentrations increase and the Y concentration decreases in the vicinity of the membrane and consequently their transport occurs. If the electrolyte is not artificially mixed, diffusion and natural convection are the governing transport processes. The transport of individual components is characterized by the appropriate mass fluxes. Among the material fluxes, material balance with respect to Y must hold,

$$J_{\mathrm{Y}} + 2\, J_{\mathrm{AgY_2}} = 0 \tag{21}$$

and the charge balance (since X, Y and AgY_2 carry a single negative charge) must also be maintained $J_X + J_Y + J_{AgY_2} = 0$, giving

$$J_{AgY_2} = J_X \tag{22}$$

The material fluxes are expressed by the product of the transport constants, κ_X, κ_Y, and κ_{AgY_2}, and of the differences between the substance concentrations far away from the membrane c_X, c_Y, and c_{AgY_2} and the concentrations in the close vicinity of the membrane $c_X(0)$, $c_Y(0)$, and $c_{AgY_2}(0)$. The relationship then becomes: $(c_{AgY_2} = 0)$

$$\kappa_Y [c_Y - c_Y(0)] - 2\,\kappa_{AgY_2} c_{AgY_2}(0) = 0 \tag{23}$$

$$\kappa_{AgY_2} c_{AgY_2}(0) = \kappa_X [c_X(0) - c_X] \tag{24}$$

Our purpose is to calculate $c_X(0)$, which will be substituted in the membrane potential equation (9):

$$\Delta\varphi_M = \frac{RT}{F} \ln \frac{c_X(0)}{c_X(1)} \tag{25}$$

By mean of eqns. (23) and (24), $c_{AgY_2}(0)$ and $c_Y(0)$ are calculated and are substituted into the modified equation (20):

$$K = \frac{c_{AgY_2}(0) c_X}{c_Y^2(0)} \tag{26}$$

In this way, the equation for $c_X(0)$ is obtained

$$K = \frac{\left[\dfrac{\kappa_X}{\kappa_{AgY_2}} c_X(0) - \dfrac{\kappa_X}{\kappa_{AgY_2}} c_X\right] c_X(0)}{\left[-\dfrac{2\kappa_X}{\kappa_Y} c_X(0) + \dfrac{2\kappa_X}{\kappa_Y} c_X + c_Y\right]^2} \tag{27}$$

This equation is further simplified assuming $K \gg 1$, resulting in the equation

$$c_X(0) = c_X + \frac{\kappa_Y}{2\kappa_Y} c_Y = c_X + \tfrac{1}{2}(D_Y/D_X)^\beta c_Y \tag{28}$$

where D_X and D_Y are the diffusion coefficients of X and Y, respectively, and β is a constant with a value of about 0.6 to 0.75, depending on the natural convection character at the vertically placed surface[286]. In the original work by Jaenicke[298], $\beta = 1$; for Jaenicke, according to the Nernst concept, considers the thickness of the diffusion layer as being independent of the diffusion coefficient. The selectivity constant $K_{X,Y}^{Pot} = \frac{1}{2}(D_Y/D_X)^\beta \approx \frac{1}{2}$, and for the membrane potential,

$$\Delta\varphi_M = \frac{RT}{F} \ln \frac{c_X + \frac{1}{2}(D_Y/D_X)^\beta c_Y}{c_X(1)} \tag{29}$$

A somewhat different relationship was obtained by Tóth and Pungor[654]. One cannot completely agree with a further solution[176].

2. *The Donnan potential*[142]

The liquid junction potential formed during unconstrained diffusion at the interface of two electrolytes (see para 1, p. 339) is one of the two limiting cases which may occur at an electrochemical membrane. The other limiting case occurs when the membrane completely prevents diffusion of at least one ion between spaces 1 and 2. Such a potential is called the Donnan potential. Let us consider a system where sodium chloride is present in solution 2, in concentration c_2, and in solution 1 is the sodium salt of an anion which cannot (*e.g.* because of its size) diffuse into solution 2. This system is not in equilibrium; consequently diffusion of sodium chloride from solution 2 into solution 1 takes place, until the concentration in solution 2 decreases to the equilibrium value, $c_2 - x$. Of course, the chloride ion concentrations on the two sides of the membrane cannot balance. Connected with chloride ion transfer through the membrane is the transfer of the same number of positive ions, for which a concentration difference thus forms, of the opposite sign to that of chloride ion concentrations. In the equilibrium state, the electrochemical potentials of the components present in both solutions are equal. (This relation is more generally valid, since it is obeyed even in cases when only the interface is in equilibrium, while the system as a whole is not in equilibrium.)

$$\tilde{\mu}_{\mathrm{Na^+}}(1) = \tilde{\mu}_{\mathrm{Na^+}}(2) \qquad \tilde{\mu}_{\mathrm{Cl^-}}(1) = \tilde{\mu}_{\mathrm{Cl^-}}(2)\,. \tag{30}$$

Hence, for the Donnan potential, for the case of dilute solutions, we have:

$$\varphi_2 - \varphi_1 = \Delta\varphi_{\mathrm{D}} = \frac{RT}{F} \ln \frac{c_{\mathrm{Na^+}}(1)}{c_{\mathrm{Na^+}}(2)}\,. \tag{31}$$

Simultaneously, the equation

$$\Delta\varphi_{\mathrm{D}} = \frac{RT}{F} \ln \frac{c_{\mathrm{Cl^-}}(2)}{c_{\mathrm{Cl^-}}(1)} \tag{32}$$

is valid, so that, from both equations, it follows that

$$c_{\mathrm{Na^+}}(1)\, c_{\mathrm{Cl^-}}(1) = c_{\mathrm{Na^+}}(2)\, c_{\mathrm{Cl^-}}(2) \tag{33}$$

which is the basic relation for the Donnan equilibrium. It must be pointed out that the condition of dilute solutions is introduced for two reasons: first to be able to substitute concentrations for activities, and, secondly, to be able to neglect the pressure effect on the chemical potentials of the components, whose electrochemical potentials appear in eqn. (30). As a consequence of different ionic concentrations in solutions 1 and 2, the osmotic pressures in these solutions are not identical and their difference must be in equilibrium counterpoised by the external pressure. For the derivation taking the effect of pressure into account, see ref. 224 or ref. 327, p. 191–193.

The Donnan potential must be measured in such a way that the potential difference between the two solutions is measured (which cannot be done precisely, but with an acceptable approximation, *e.g.* with the help of two saturated calomel electrodes, as will be shown in para 1, p. 342). If two identical electrodes, sensitive to the same kind of ion (*e.g.* two silver chloride electrodes) were placed in solutions 1 and 2 and the resulting electromotive force of the cell formed without transport were measured,

$$E = E_2 + \Delta\varphi_{\mathrm{D}} - E_1 \tag{34}$$

(E_2 and E_1 are the respective electrode potentials of the two silver chloride electrodes), we would find that $E = 0$. This follows both from eqn. (31), which shows that $\Delta\varphi_{\mathrm{D}}$ and $E_2 - E_1$ have the same absolute value, but opposite signs, and also from the assumption that the system is in equilibrium and consequently cannot produce electrical work.

If the membrane, which separates the two solutions in the case of the Donnan equilibrium, were removed without mixing the solutions, the electric potential difference between them would be maintained, momentarily, at the same value as that in the presence of the membrane. Thus, for the Donnan potential, a membrane is not necessary, only the appropriate distribution of ions; this has also been proven experimentally[273].

Membrane potentials in the presence of diffusion potential

If transport of ions at different velocities occurs within the membrane, a diffusion potential can be formed. First we shall consider the diffusion potential at the boundary between two solutions with different composition, *i.e.* the liquid junction potential. Its properties are important both for the theory of membrane potentials and for experimental techniques in work with ion-selective electrodes.

1. *Liquid junction potentials*

Let us consider a case when two solutions of electrolytes with different composition are directly in contact or that this contact is ensured by a porous diaphragm which is permeable for all kinds of ions present in both electrolytes.

The only process taking place in the membrane is the diffusion of various components of the two solutions. Because of the different diffusion rates of the ions, an electric potential gradient appears within the membrane (the so-called diffusion potential gradient). Between the two solutions, which are assumed to be of uniform composition everywhere outside the membrane, a potential difference is formed, called the liquid junction potential, $\Delta\varphi_L$.

To the mass flux of each component, J_i, when it is accompanied by charge transport ($z_i \neq 0$), corresponds a partial current density

$$j_i = z_i F J_i\,. \tag{35}$$

If no electric current flows through the liquid junction (*e.g.* if no external voltage is applied), the total current density, j, is given by

$$j = \sum_i j_i = 0 \tag{36}$$

After substitutions from eqns. (4) and (35) into eqn. (36) and rearrangement, we get

$$\frac{\mathrm{d}\varphi}{\mathrm{d}x} = -\frac{RT}{F}\,\frac{\sum_i z_i U_i \mathrm{d}c_i/\mathrm{d}x}{\sum_j z_j^2 U_j c_j} = -\frac{RT}{F}\,\frac{\sum_i z_i U_i c_i \mathrm{d}\ln c_i/\mathrm{d}x}{\sum_j z_j^2 U_j c_j} = -\frac{RT}{F}\sum_i \frac{t_i}{z_i}\,\frac{\mathrm{d}\ln c_i}{\mathrm{d}x} \tag{37}$$

where t_i is the transference number of the ith component

$$t_i = z_i^2 U_i c_i \Big/ \sum_j z_j^2 U_j c_j \tag{38}$$

The liquid junction potential is given by the relation[507,508]

$$\Delta\varphi_L = \varphi_2 - \varphi_1 = -\frac{RT}{F}\int_1^2 \sum_i \frac{t_i}{z_i}\,\mathrm{d}\ln c_i \tag{39}$$

where the integration limits are related to the composition of solutions 1 and 2. In rigorous formulation, it is necessary to substitute activities, a_i, for concentrations, c_i. The value of $\Delta\varphi_L$ generally depends on the nature of the functions of x describing the concentrations, c_i, and consequently also on t_i. The simplest case arises when a single electrolyte, with different concentrations, c_1 and c_2, is on both sides of the membrane. Then:

$$t_+ = \frac{z_+ U_+}{z_+ U_+ - z_- U_-} \quad \text{and} \quad t_- = \frac{-z_- U_-}{z_+ U_+ - z_- U_-} \tag{40}$$

where the subscripts + and − denote the values for the cation and anion of the electrolyte, respectively. For $\Delta\varphi_L$, we obtain

$$\Delta\varphi_L = -\frac{RT}{F}\left(\frac{t_+}{z_+} + \frac{t_-}{z_-}\right)\ln\frac{c_2}{c_1} = -\frac{RT}{F}\,\frac{z_+ - (z_+ - z_-)t_+}{z_+ z_-}\ln\frac{c_2}{c_1} \tag{41}$$

In this case, the liquid junction potential does not depend on the distribution of the ion concentrations within the liquid junction.

A general solution of the integral in eqn. (39) is impossible, and therefore certain assumptions must be made concerning the dependence of ion concentrations on the x-coordinate within the liquid junction. The approximate Henderson solution[262,263] is very frequently used, in which it is assumed that the concentrations of ions within the liquid junction vary linearly with x, between the values in the two solutions. Thus we have:

$$c_i(x) = c_i(p) + [c_i(q) - c_i(p)]\,x/d \tag{42}$$

On substituting into eqn. (39), we obtain

$$\varphi_2 - \varphi_1 = -\frac{RT}{F}\int_0^d \frac{\sum_i z_i U_i\{[c_i(q)-c_i(p)]x/d + c_i(p)\}}{\sum_j z_j^2 U_j\{[c_j(q)-c_j(p)]x/d + c_j(p)\}}\,\mathrm{d}\ln\{[c_i(q)-c_i(p)]x/d + c_i(p)\}$$

$$= -\frac{RT}{F}\,\frac{\sum_i z_i U_i[c_i(q)-c_i(p)]}{\sum_i z_i^2 U_i[c_i(q)-c_i(p)]}\ln\frac{\sum_i z_i^2 U_i c_i(q)}{\sum_i z_i^2 U_i c_i(p)} \tag{43}$$

where $d = q - p$ is the thickness of the liquid junction.

The Henderson formula expresses the properties of liquid junctions which can be characterized as "mixture type". Perhaps the closest case to this model is the liquid junction with free diffusion, shown in Fig. 2. The uncertainty in determining the liquid junction potential is, as stated by Ives and Janz[295], about 1–2 mV.

Integration of eqn. (39) was carried out by Planck[507,508] (and for a more general case by Schlögl[580]) for the case of the so-called "constrained diffusion", to which correspond the liquid junctions given in Fig. 3. Differing from Henderson's solution, Planck's solution is not expressed by a closed formula. His whole procedure is given, for example, in MacInnes' textbook[367]. It should be noted that, since the liquid junction potential depends on the distribution of ionic species within this junction, it will exhibit values varying with time, from the instant of initial contact of the electrolytes up to the establishment of a steady state.

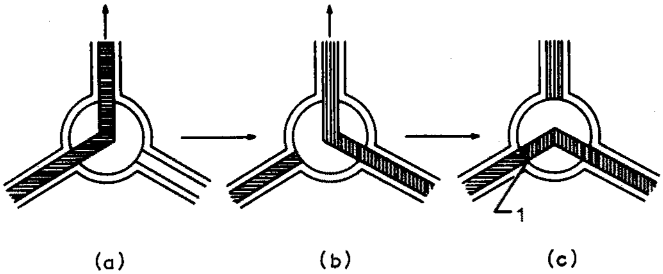


Fig. 2. Liquid junction with free diffusion. (a) The tested solution is drawn (in the direction of the arrow) into the stop-cock; (b) the saturated KCl solution from a liquid bridge is drawn into the stop-cock; (c) by turning the stop-cock, the test solution–liquid bridge 1 liquid junction is formed. After Mattock and Band[383]. With permission of Marcel Dekker Inc.

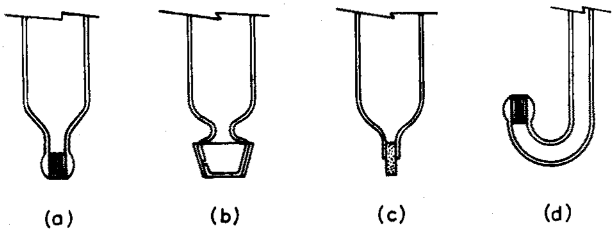


Fig. 3. Various types of liquid junction with limited diffusion. (a) Ceramic plug; (b) ground-glass jacket; (c) asbestos wick; (d) U-shaped connection with a ceramic plug. After Mattock and Band[383]. With permission of Marcel Dekker Inc.

If single uni-univalent electrolytes with a common cation or anion are present on both sides of the liquid junction, the concentrations of the electrolytes being identical (even in the membrane surface, at places $x=p$ and $x=q$), *e.g.*

$$\begin{array}{l|l} 0.1\ M\ \mathrm{KCl} & 0.1\ M\ \mathrm{HCl} \\ \text{solution 1} & \text{solution 2} \end{array}$$

then eqn. (43) is reduced to

$$\Delta\varphi_{\mathrm{L}} = \mp\frac{RT}{F}\ln\frac{U_{+}(2)+U_{-}(2)}{U_{+}(1)+U_{-}(1)} = \mp\frac{RT}{F}\ln\frac{\Lambda(2)}{\Lambda(1)}, \tag{44}$$

where symbols 1 and 2 denote the electrolytes of solutions 1 and 2, respectively, and Λ are the equivalent conductivities, according to Lewis and Sargent[349], at the given electrolyte concentration. The minus sign is valid for the case when the electrolytes have a common anion, the plus sign for a common cation. This equation fits the experimental data very well, as is shown in Table I[349].

For a detailed discussion of liquid junction potentials see refs. 31, 119, 223, 295, 367, 383. Good results with the Henderson formula have been reported[42,600].

An ideal potentiometric measurement, especially in analytical chemistry, would be that in which the reference electrode potential is fixed, with only the indicator electrode potential changing with changes in the solution composition. This could be achieved if the liquid junction potential could be neglected. Such a case arises only when the solutions of both electrodes contain a certain electrolyte at a concentration considerably outweighing that of all other electrolytes. Then a change

TABLE I

THE LIQUID JUNCTION POTENTIAL VALUES FOR SOME SOLUTIONS, ACCORDING TO LEWIS AND SARGENT[349]

(All values at 25°)

Liquid junction			
Electrolyte 2	*Electrolyte 1*	$\Delta\varphi_{L\,exp.}$ (*mV*)	$\Delta\varphi_{L\,calc.}$ (*mV*)
0.1 *M* HCl	0.1 *M* KCl	−26.78	−28.52
0.1 *M* HCl	0.1 *M* KCl	−33.09	−33.38
0.1 *M* KCl	0.1 *M* NaCl	− 6.42	− 4.86
0.1 *M* NaCl	0.1 *M* NH_4Cl	+ 4.21	+ 4.81
0.01 *M* HCl	0.01 *M* KCl	−25.73	−27.48
0.01 *M* KCl	0.01 *M* NaCl	− 5.65	− 4.54

in the concentration of some minor species in the indicator electrode solution causes only a negligible change in liquid junction potential.

This procedure can, of course, rarely be carried out. An acceptable procedure would also be one, in which the cell, the e.m.f. of which is measured, would contain a liquid junction, but with a constant liquid junction potential. This can be achieved, *e.g.* in fluoride determinations with the lanthanum fluoride ion-selective electrode, by adding a constant amount of the rather concentrated buffer, TISAB (see p. 371) to the analyzed solution. Then the liquid junction potential is practically only a function of the composition of the reference electrode electrolyte and that of the buffer.

Another, less precise, but generally used procedure is based on a bridge between the solutions of the indicator and the reference electrode, which is usually filled with a saturated potassium chloride solution. If the reference electrode is, for example, a saturated calomel electrode, then no other bridge is required. When the liquid bridge is used, the fact that the mobilities of potassium and chloride ions are roughly the same is utilized. In the case when this solution is in contact with a much more dilute electrolyte, the liquid junction potential has, as follows from the Henderson formula, a negligible value. If, however, the saturated KCl solution is in contact with a rather concentrated electrolyte solution, the cation of which has a considerably different mobility from the anion, then the liquid junction potential can reach rather high values[75] (*e.g.* for the junction 3.5 *M* KCl || 1 *M* NaOH, $\Delta\varphi_L$ is 10.5 mV). For biological measurements, liquid bridges filled with agar gel, saturated with potassium chloride, are favoured.

2. *Potentials of permselective membranes*[261,337,619]

No assumption concerning the nature of the electrochemical membrane was made in the derivation of relations for the Donnan potential. However, one possibility for preventing diffusion of an ion is the use of a membrane with porous structure, through which for example, particles with larger dimensions cannot penetrate. Another possibility for preventing diffusion is the presence of charges of uniform sign firmly bound on the walls of the membrane pores, for example, by adsorption of a surface-active ion or the presence of ionizable groups which are a part of the membrane structure. Especially important materials for this type of membrane are synthetic polymers with ionized groups[261] (*e.g.* with sulphonic acid groups or with quarternary nitrogen).

As a consequence of fixed charges on the pore surface, a diffuse electrical double layer is formed in the vicinity of the pore surface[619], *i.e.* a region of the electrolyte in which a space charge is formed by an excess of ions with the opposite sign to that of the fixed charges. If this region is substantially thinner than the pore radius, then the presence of fixed charges will not affect the permeability of ions through the membrane. However, if the diffuse electric double layer thickness is comparable with the pore radius, or if ions of the opposite sign fill the pore completely, then the membrane becomes permselective for the ions filling the pores; ions of the opposite sign (*i.e.* of sign identical with that of the fixed charges) permeate through the membrane with difficulty[28,620]. By a change in the pore size (or by a change in the diffuse electric double layer thickness, which can be caused by a change in the electrolyte concentration), the membrane properties can change from those of a liquid junction to those of a permselective membrane and finally to those of a Donnan-type membrane. As Michaelis has shown[394,396], the liquid junction potential and the Donnan potential are, in simple cases, the limiting values of the membrane potential.

Let us consider a system where solutions 1 and 2 contain different concentrations of the same electrolyte, A^+B^-:

$$\begin{array}{c|c} A^+B^- & A^+B^- \\ c_1 & c_2 \end{array}$$

If the membrane is permeable for both kinds of ions, then for dilute solutions we have

$$\Delta\varphi_M = \Delta\varphi_L = (2t_- - 1)\frac{RT}{F}\ln\frac{c_2}{c_1} \tag{45}$$

If it is nonpermeable for the anion, t_- equals zero and

$$\Delta\varphi_M = \frac{RT}{F}\ln\frac{c_1}{c_2} \tag{46}$$

which is the simple Donnan potential. If it is nonpermeable for the cation, t_- equals unity and

$$\Delta\varphi_M = \frac{RT}{F}\ln\frac{c_2}{c_1} \tag{47}$$

Michaelis has characterized intermediate cases by the assumption that the anion and cation transport numbers have different values within the membrane, t'_+ and t'_-, from those in the electrolyte, t_+ and t_-; thus

$$\Delta\varphi_M = (t'_+ - t'_-)\frac{RT}{F}\ln\frac{c_1}{c_2} \tag{48}$$

The electric potential distribution within the membrane in intermediate cases was qualitatively characterized by Sollner[620] with the help of a three-regions concept: in the membrane–solution interfaces potential differences are formed (following from eqns. 2); within the membrane, a liquid junction potential appears because of the diffusion of ions through the membrane. This concept was quantitatively expressed by Teorell[643] and by Meyer and Sievers[392,393]. In the simplest case, the system contains free ions A^+ and B^- and a fixed ion X^+ at concentration c_X. The concentrations of ions A^+ and B^-, c_+ and c_-, respectively, at the ends of the membrane, are determined from relations analogous to eqn. (33)

$$\begin{aligned} c_+(p)\,c_-(p) &= c_1^2 \\ c_+(q)\,c_-(q) &= c_2^2 \end{aligned} \tag{49}$$

Inside the membrane, the electroneutrality condition applies

$$c_+ + c_X = c_- \tag{50}$$

On substituting from eqn. (50) into eqns. (49), we obtain

$$\begin{aligned} c_+(p) &= c_X\{(\tfrac{1}{4}+c_1^2/c_X^2)^{\frac{1}{2}}-\tfrac{1}{2}\} \\ c_-(p) &= c_X\{(\tfrac{1}{4}+c_1^2/c_X^2)^{\frac{1}{2}}+\tfrac{1}{2}\} \end{aligned} \tag{51}$$

and analogous expressions for $c_+(q)$ and $c_-(q)$, in which c_2 appears instead of c_1. The values $c_+(p)$, $c_-(p)$, $c_+(q)$, and $c_-(q)$, and c_X appear as concentration values at the boundaries of the liquid junction, which are substituted into eqn. (43). In this way, the following relation is obtained

$$\begin{aligned} \varphi(q)-\varphi(p) &= -\frac{U_+-U_-}{U_++U_-}\,\frac{RT}{F}\ln\frac{U_+c_X\{(\frac{1}{4}+c_2^2/c_X^2)^{\frac{1}{2}}-\frac{1}{2}\}+U_-c_X\{(\frac{1}{4}+c_2^2/c_X^2)^{\frac{1}{2}}+\frac{1}{2})}{U_+c_X\{(\frac{1}{4}+c_1^2/c_X^2)^{\frac{1}{2}}-\frac{1}{2}\}+U_-c_X\{(\frac{1}{4}+c_1^2/c_X^2)^{\frac{1}{2}}+\frac{1}{2})} = \\ &= -\frac{U_+-U_-}{U_++U_-}\,\frac{RT}{F}\ln\frac{(U_++U_-)c_X\{(\frac{1}{4}+c_2^2/c_X^2)^{\frac{1}{2}}-\frac{1}{2}\}+U_-c_X}{(U_++U_-)c_X\{(\frac{1}{4}+c_1^2/c_X^2)^{\frac{1}{2}}-\frac{1}{2}\}+U_-c_X} = \\ &= -\frac{U_+-U_-}{U_++U_-}\,\frac{RT}{F}\ln\frac{(U_++U_-)c_+(q)+U_-c_X}{(U_++U_-)c_+(p)+U_-c_X} \end{aligned} \tag{52}$$

In calculation of the total membrane potential, the Donnan potential between solution 2 and the membrane interior at the point, $x=q$, $\Delta\varphi_D(q)$, and the Donnan potenal between the membrane interior at the point, $x=p$, and solution 1 must be taken into account. It must be borne in mind that the interface, permeable only for certain ions (discussed above in eqn. (30) *et seq.*) and represented by an unspecified membrane, is in the present case replaced by the membrane surface. The total membrane potential, $\Delta\varphi_M$, is given by the following relation, which will also be used later:

$$\begin{aligned} \Delta\varphi_M = \varphi(2)-\varphi(1) &= \varphi(2)-\varphi(q)+\varphi(q)-\varphi(p)+\varphi(p)-\varphi(1) \\ &= \Delta\varphi_D(2)+\varphi(q)-\varphi(p)+\Delta\varphi_D(1) \end{aligned} \tag{53}$$

From equations analogous to (31) and (33) and from eqns. (52) and (53), we can obtain

$$\Delta\varphi_M = \frac{RT}{F}\left[\underbrace{\ln\frac{c_+(q)c_1}{c_+(p)c_2}}_{\text{Donnan term}} - \underbrace{\left(\frac{U_+-U_-}{U_++U_-}\right)\ln\left[\frac{(U_++U_-)c_+(q)+U_-c_X}{(U_++U_-)c_+(p)+U_-c_X}\right]}_{\text{Henderson term}}\right] \tag{54}$$

These relationships were made more precise by Teorell in later papers[640-642,644], in which he starts from the Planck concept of the liquid junction potential.

3. *Solid-state ion-exchange membranes interacting with two kinds of ions: The diffusion potential in the membrane*[113,114,160,309]

In this paragraph, a compact ion-exchange membrane with a concentration of active (anionic) sites, C_0, is considered. All sites are equivalent and each carries a single negative charge. The membrane is permeable only for cations. It is assumed that two kinds of univalent cations, J^+ and K^+, are present in the solutions on both sides of the membrane, simultaneously enter the membrane, and associate with its anion centres as so-called "counter-ions". An ion-exchange reaction takes place between the ions in solution and in the membrane

$$J^+(s) + K^+(m) = J^+(m) + K^+(s) \tag{55}$$

where the symbol s denotes ions in the electrolyte and m those in the membrane. The activities of ions J^+ and K^+ in solution 1 are $a_J(1)$ and $a_K(1)$, and in solution 2, $a_J(2)$ and $a_K(2)$, respectively, and their concentrations in the membrane are C_J and C_K, respectively. The concentrations in the membrane are, of course, functions of the location between the two membrane interfaces. In the instant of contact of the membrane with an electrolyte containing ions J^+ and K^+, ion exchange in the membrane surface takes place. Thus non-equilibrium concentrations of these particles in solution at the membrane surface are formed. Since, however, diffusion inside the membrane is much slower than that in solution, a practically constant concentration of J^+ and K^+ is soon established throughout the solution.

At the membrane interface (*e.g.* at $x = p$), the thermodynamic equilibrium condition holds for the above exchange reaction

$$\tilde{\mu}_J(1) + \tilde{\mu}_K(p) = \tilde{\mu}_K(1) + \tilde{\mu}_J(p) \tag{56}$$

from which it follows (on the assumption of ideal counter-ion behaviour in the membrane) for the equilibrium ion-exchange constant, K_{KJ}, that

$$K_{KJ} = \frac{C_J(p)\, a_K(1)}{C_K(p)\, a_J(1)} = \exp \frac{\mu_J^0(s) + \mu_K^0(m) - \mu_J^0(m) - \mu_K^0(s)}{RT}\,. \tag{57}$$

Simultaneously, the equations

$$\begin{aligned} \tilde{\mu}_J(1) &= \tilde{\mu}_J(p) \\ \tilde{\mu}_K(1) &= \tilde{\mu}_K(p) \end{aligned} \tag{58}$$

are valid, from which it follows that

$$\begin{aligned} \Delta\varphi_D(1) = \varphi(p) - \varphi(1) &= [\mu_J^0(s) - \mu_J^0(m)]/F + (RT/F)\ln(a_J(1)/C_J(p)) = \\ &= [\mu_K^0(s) - \mu^0{}_K(m)]/F + (RT/F)\ln(a_K(1)/C_K(p)) \end{aligned} \tag{59}$$

Different concentrations of J^+ and K^+ at points $x = p$ apd $x = q$ lead to ion transport and formation of a diffusion potential. The diffusion potential within the membrane phase is expressed by means of the Henderson equation (43), similar to the treatment by Meyer and Sievers[392,393] and Teorell[643] for permselective membranes. The values U_J and U_K denote the mobilities of the ions J^+ and K^+, respectively, within the membrane; the ionic centres are assumed to be immobile. The diffusion potential inside the membrane is given by the relation

$$\varphi(q) - \varphi(p) = -\frac{RT}{F} \ln\left[\frac{(U_J/U_K)\, C_J(q) + C_K(q)}{(U_J/U_K)\, C_J(p) + C_K(p)}\right] \tag{60}$$

For the total membrane potential, $\Delta\varphi_M$, eqn. (53) is used, into which are substituted eqns. (59) and (60), the analogous relation for $\Delta\varphi_D(2)$ (it must, of course, be kept in mind that $\Delta\varphi_D(2)$ is defined as the difference $\varphi(2)-\varphi(q)$), and also eqn. (57). In this way, we obtain the relation

$$\Delta\varphi_M = \underbrace{\frac{RT}{F}\ln\frac{C_J(q)\,a_J(1)}{C_J(p)\,a_J(2)}}_{\text{the Donnan term}} - \underbrace{\frac{RT}{F}\ln\left[\frac{(U_J/U_K)C_J(q)+C_K(q)}{(U_J/U_K)C_J(p)+C_K(p)}\right]}_{\text{the Henderson term}} \tag{61}$$

$$= \frac{RT}{F}\ln\left[\frac{(U_J/U_K)K_{KJ}a_J(1)+a_K(1)}{(U_J/U_K)K_{KJ}a_J(2)+a_K(2)}\right]$$

The selectivity constant is given by the formula

$$K_{KJ}^{\text{Pot}} = (U_J/U_K)K_{KJ} \tag{62}$$

This equation is analogous to the Goldman–Hodgkin–Katz equation[206,274–276,311], which was formulated for biological membranes based on the assumption of a constant electric field strength within the membrane. The same result as that in the present review was obtained by Eisenman and co-workers (see ref. 160), who solved the appropriate Nernst–Planck equations for transport inside the membrane. They also gave a solution for the special case of the so-called n-type membrane, where the following relation holds between the ion activity in the membrane and its concentration:

$$\mathrm{d}\ln a_J(m)/\mathrm{d}\ln C_J = \mathrm{d}\ln a_K(m)/\mathrm{d}\ln C_K = n \tag{63}$$

where n is independent of the distance from the membrane surface so that

$$a_J(m) \sim C_J^n \tag{64}$$

is valid. The resulting expression for the membrane potential is then

$$\Delta\varphi_M = \frac{nRT}{F}\ln\frac{(U_J/U_K)K_{KJ}^{1/n}a_J(1)^{1/n}+a_K(1)^{1/n}}{(U_J/U_K)K_{KJ}^{1/n}a_J(2)^{1/n}+a_K(2)^{1/n}} = \tag{65}$$

$$= \frac{nRT}{F}\ln\frac{a_K(1)^{1/n}+(K_{KJ}^{\text{Pot}})^{1/n}a_J(1)^{1/n}}{a_K(2)^{1/n}+(K_{KJ}^{\text{Pot}})^{1/n}a_J(2)^{1/n}}$$

An important drawback of these solutions lies in the fact that they assume a stationary state in the distribution of the diffusion potential across the entire membrane, which is unattainable because of its large thickness and the slowness of transport through the solid phase (this assumption is, however, justified for very thin cell membranes). Another shortcoming is the assumption of constant mobilities of ions in the membrane; the mobility of one ion is notably affected by the presence of other ions. Mobilities of ions close to the membrane surface will probably also be affected by the solvent which solvates the adjacent layer to a varying degree.

4. *Liquid membranes with neutral carrier*

In this case, the liquid membrane, immiscible with solutions 1 and 2, contains a dissolved carrier, V, (usually an electroneutral macrocyclic compounds, see p. 385), which forms a complex with ions determining the membrane potential. This carrier is practically completely bound into the complex with univalent cations J^+ and K^+. Cation exchange between an aqueous solution in contact with the membrane and the membrane itself is fast, while anion transfer across the solution–membrane interface is slow[76]. Then the procedure given in paragraph 3 above can be used to solve this case. The ion-exchange reaction will be (*cf.* eqn. 55)

$$J^+(s) + VK^+(m) \rightleftharpoons VJ^+(m) + K^+(s) \tag{66}$$

where VJ^+ and VK^+ denote the complexes of ions J^+ and K^+ with the carrier, V, respectively. The corresponding ion-exchange equilibrium constant, K_{KJ}, is given by the relation (at the $x=p$ interface)

$$K_{KJ} = \frac{a_{JV}(p)\, a_K(1)}{a_{KV}(p)\, a_J(1)} = \exp \frac{\mu_J^0(s) + \mu_{KV}^0(m) - \mu_{JV}^0(m) - \mu_K^0(s)}{RT} \tag{67}$$

The contact equilibria are

$$\begin{aligned} \tilde{\mu}_J(1) &= \tilde{\mu}_{JV}(p) \\ \tilde{\mu}_K(1) &= \tilde{\mu}_{KV}(p) \end{aligned} \tag{68}$$

so that the potential difference between the membrane and the solution 1 is given by the relation

$$\Delta\varphi_D(1) = (\mu_J^0(s) - \mu_{JV}^0(m))/F + \frac{RT}{F} \ln \frac{a_J(1)}{a_{JV}(p)} \tag{69}$$

$$= (\mu_K^0(s) - \mu_{KV}^0(m))/F + \frac{RT}{F} \ln \frac{a_K(1)}{a_{KV}(p)} \tag{69}$$

Since the macrocyclic ligands themselves have a large volume and encircle the complexed ion, the size and shape of the resulting structure changes very little among various ions, and the mobilities of the various complexes also differ only slightly[632,633]. For this reason, the diffusion potential across the membrane may be practically neglected (*i.e.* $\varphi(q) = \varphi(p)$). The ion concentration in the membrane is determined by the total concentration of the macrocyclic ligand, c_V.

$$c_{JV}(p) + c_{KV}(p) = c_V \tag{70}$$

It is assumed that the complex solutions in the membrane are dilute and therefore concentrations $c_{JV}(p)$ and $c_{KV}(p)$ can be substituted for activities $a_{JV}(p)$ and $a_{KV}(p)$, respectively, in eqns. (67) and (69). Then the expression for the membrane potential is obtained from eqns. (67), (69), (70) and analogous relations for the dependences at the other interface $(x=q)$:

$$\Delta\varphi_M = \Delta\varphi_D(1) + \Delta\varphi_D(2) = \frac{RT}{F} \ln \frac{K_{KJ} a_J(1) + a_K(1)}{K_{KJ} a_J(2) + a_K(2)} \tag{71}$$

The selectivity constant is thus given by the relationship:

$$K_{KJ}^{Pot} = K_{KJ} \tag{72}$$

Ion transfer from an aqueous solution into a complex in a solvent forming the membrane can, under certain simplifying assumptions, which will be discussed in detail on p. 392 *et seq.* (the same solvation of all complexes in the membrane, the same interaction of ions with the interior of the macrocyclic compound in water and in the membrane solvent), be reduced to the difference of the interaction energies of the ion with water and with the interior of the macrocyclic compound. For the standard chemical potential term in eqn. (67), we can then write

$$\begin{aligned} &\mu_J^0(s)+\mu_{KV}^0(m)-\mu_{JV}^0(m)-\mu_K^0(s) \\ &\quad\approx \mu_{KV}^0(s)-\mu_K^0(s)-\mu_V^0(s)-(\mu_{JV}^0(s)-\mu_J^0(s)-\mu_V^0(s)) \\ &\quad= RT\ln K_{KV}-RT\ln K_{JV} \end{aligned} \tag{73}$$

where K_{JV} and K_{KV} are the stability constants of the complexes JV^+ and KV^+ respectively in aqueous solution, and $\mu_V^0(s)$ is the standard chemical potential of the macrocyclic compound in water. With regard to these simplifications, the selectivity constant is then given by the approximate relation[160,162,163,632,633]

$$K_{KJ}^{Pot} \approx \frac{K_{KV}}{K_{JV}} \tag{74}$$

For a very thin membrane, the thickness of which does not exceed the dimension of the effective thickness of the diffuse electric double layer (*i.e.* the so-called Debye length, see *e.g.* ref. 327, p. 21), an expression for the membrane potential determined by complexes of ions with macrocyclic carriers has been derived by Ciani, Eisenman, and Szabó[99,160,162,163,633]. They assume that the electroneutrality condition is not valid throughout the entire membrane phase. This model applies to the case of black bilayer membranes[414,415].

5. *Liquid membranes with dissolved charged ion exchangers*[155,160,575–577,678]

The membrane contains a dissolved anion exchanger which is insoluble in solutions 1 and 2. Let us consider again two kinds of cations in each electrolyte, which associate with anion-exchange sites, S^-, in the membrane, according to equations

$$\begin{aligned} J^+ + S^- &= JS \\ K^+ + S^- &= KS \end{aligned} \tag{75}$$

On the assumption that the components behave ideally in the membrane phase, then for the association constants in the membrane phase, we have:

$$K_{JS} = \frac{C_{JS}}{C_J C_S}, \qquad K_{KS} = \frac{C_{KS}}{C_K C_S} \tag{76}$$

It should be noted that in solution concentration gradients of J^+ and K^+ form during practical experiments on ion-exchange processes in a liquid membrane; the elimination of these depends on natural convection in solution (the membrane is usually fixed by means of a porous medium so that natural convection in it is suppressed). The convection effect on conditions in the solution leads, however, to low precision in determining selectivity constants.

The electroneutrality condition applies within the membrane phase

$$C_S = C_K + C_J \tag{77}$$

Equilibria, characterized by Donnan potentials, *e.g.* by relation (59) for the interface $x=p$, are formed at the interfaces. Simultaneously, the following relation holds for both ions

$$\frac{a_J(1)k_J}{C_J(p)}=\frac{a_K(1)k_K}{C_K(p)} \tag{78}$$

where

$$k_J=\exp[-(\mu_J^0(m)-\mu_J^0(s))/RT] \quad \text{and} \quad k_K=\exp[-(\mu_K^0(m)-\mu_K^0(s))/RT]$$

which also follows from eqn. (59). Further, (with respect to eqn. (78)), the equation

$$\frac{a_J(1)k_J}{C_J(p)}=\frac{a_J(1)k_J+a_K(1)k_K}{C_J(p)+C_K(p)}=\frac{a_J(1)k_J+a_K(1)k_K}{C_S(p)} \tag{79}$$

is valid. Hence, a relation for $C_J(p)$ and an analogous relation for $C_K(p)$ follow

$$C_J(p)=\frac{C_S(p)a_J(1)k_J}{a_J(1)k_J+a_K(1)k_K} \tag{80}$$

$$C_K(p)=\frac{C_S(p)a_K(1)k_K}{a_J(1)k_J+a_K(1)k_K}$$

On substituting these equations into eqn. (59), we obtain a relation for $\Delta\varphi_D(1)$:

$$\Delta\varphi_D(1)=-\frac{RT}{F}\ln\frac{C_S(p)}{a_J(1)k_J+a_K(1)k_K} \tag{81}$$

In a similar way, we obtain an expression for $\Delta\varphi_D(2)$:

$$\Delta\varphi_D(2)=\frac{RT}{F}\ln\frac{C_S(q)}{a_J(2)k_J+a_K(2)k_K} \tag{82}$$

Inside the membrane, transport of particles J^+, K^+, S^-, JS, and KS occurs; the uncharged particles JS and KS are transported solely by diffusion. For the mass fluxes of all these particles, we have:

$$J_J=-U_JRT\mathrm{d}C_J/\mathrm{d}x-U_JC_JF\mathrm{d}\varphi/\mathrm{d}x \tag{83}$$

$$J_K=-U_KRT\mathrm{d}C_K/\mathrm{d}x-U_KC_KF\mathrm{d}\varphi/\mathrm{d}x \tag{84}$$

$$J_S=-U_SRT\mathrm{d}C_S/\mathrm{d}x+U_SC_SF\mathrm{d}\varphi/\mathrm{d}x \tag{85}$$

$$J_{JS}=-U_{JS}RT\mathrm{d}C_{JS}/\mathrm{d}x \tag{86}$$

$$J_{KS}=-U_{KS}RT\mathrm{d}C_{KS}/\mathrm{d}x \tag{87}$$

Since the exchange sites, S^-, do not leave the membrane in any form, their total flux in the steady state can be written as:

$$J_S+J_{JS}+J_{KS}=0 \tag{88}$$

When no electric current flows through the membrane, then

$$J_J+J_K-J_S=0 \tag{89}$$

If we substitute eqns. (83), (84), (85), (86) and (87) into eqns. (88) and (89) and eliminate C_{JS} and C_{KS} by means of eqns. (76), we obtain the following relation, after separating $\mathrm{d}C_S/\mathrm{d}x$

$$\frac{\mathrm{d}\varphi}{\mathrm{d}x} = -\frac{RT}{F} \times$$

$$\times \frac{(U_S + U_{JS}K_{JS}C_J + U_{KS}K_{KS}C_K)(U_J\mathrm{d}C_J/\mathrm{d}x + U_K\mathrm{d}C_K/\mathrm{d}x) + U_S C_S(U_{JS}K_{JS}\mathrm{d}C_J/\mathrm{d}x + U_{KS}K_{KS}\mathrm{d}C_K/\mathrm{d}x)}{(U_S + U_{JS}K_{JS}C_J + U_{KS}K_{KS}C_K)U_J C_J + (U_S + U_{JS}K_{JS}C_J + U_{KS}K_{KS}C_K)U_K C_K + (U_S + U_{JS}K_{JS}C_J + U_{KS}K_{KS}C_K)U_S C_S}$$

$$= -\frac{RT}{F}\frac{U_J\mathrm{d}C_J/\mathrm{d}x + U_K\mathrm{d}C_K/\mathrm{d}x}{U_J C_J + U_K C_K} - \frac{RT}{F}\left(\frac{U_{JS}K_{JS}\mathrm{d}C_J/\mathrm{d}x + U_{KS}K_{KS}\mathrm{d}C_K/\mathrm{d}x}{U_{JS}K_{JS}C_J + U_{KS}K_{KS}C_K} - \frac{U_J\mathrm{d}C_J/\mathrm{d}x + U_K\mathrm{d}C_K/\mathrm{d}x}{U_J C_J + U_K C_K}\right)\times$$

$$\times \frac{(U_{JS}K_{JS}C_J + U_{KS}K_{KS}C_K)U_S C_S}{(U_S + U_{JS}K_{JS}C_J + U_{KS}K_{KS}C_K)(U_J C_J + U_K C_K) + (U_S + U_{JS}K_{JS}C_J + U_{KS}K_{KS}C_K)U_S C_S} \tag{90}$$

In the case of almost *complete dissociation* ($K_{JS}C_J C_S = C_{JS} \rightarrow 0$ and analogously for C_{KS}), the second term in the above equation disappears. For the value $\varphi(q) - \varphi(p)$, eqn. (60) will then be valid. If eqn. (80) is then substituted into it, we obtain the relation

$$\varphi(q) - \varphi(p) = -\frac{RT}{F}\ln\frac{[(U_J/U_K)a_J(2)k_J + a_K(2)k_K]}{[(U_J/U_K)a_J(1)k_J + a_K(1)k_K]}\frac{C_S(q)(a_J(1)k_J + a_K(1)k_K)}{C_S(p)(a_J(2)k_J + a_K(2)k_K)} \tag{91}$$

The membrane potential is then given, with respect to eqns. (81) and (82), by the relation

$$\Delta\varphi_M = \frac{RT}{F}\ln\frac{(U_J/U_K)k_J a_J(1) + k_K a_K(1)}{(U_J/U_K)k_J a_J(2) + k_K a_K(2)} \tag{92}$$

However, in the case of *almost complete association*, we have $C_{JS} \gg C_S$ and $C_{KS} \gg C_S$. Then eqn. (90) assumes the form

$$\frac{\mathrm{d}\varphi}{\mathrm{d}x} = -\frac{RT}{F}\mathrm{d}\ln(U_J C_J + U_K C_K) - \frac{RT}{F}\frac{U_S(C_J/C_K + 1)}{(U_J + U_S)C_J/C_K + U_K + U_S}$$

$$\times \mathrm{d}\ln\frac{U_{JS}K_{JS}C_J/C_K + U_{KS}K_{KS}}{U_J C_J/C_K + U_K} \tag{93}$$

On integration, we obtain

$$\varphi(q) - \varphi(p) = -\frac{RT}{F}\left\{(1-\tau)\ln\frac{(U_J + U_S)C_J(q) + (U_K + U_S)C_K(q)}{(U_J + U_S)C_J(p) + (U_K + U_S)C_K(p)}\right.$$

$$\left. + \tau\ln\frac{U_{JS}K_{JS}C_J(q) + U_{KS}K_{KS}C_K(q)}{U_{JS}K_{JS}C_J(p) + U_{KS}K_{KS}C_K(p)}\right\} \tag{94}$$

where

$$\tau = \frac{U_S(U_{KS}K_{KS} - U_{JS}K_{JS})}{(U_J + U_S)U_{KS}K_{KS} - (U_K + U_S)U_{JS}K_{JS}} \tag{95}$$

For the membrane potential for almost complete association,

$$\Delta\varphi_M = -\frac{RT}{F}(1-\tau)\frac{(U_J + U_S)k_J a_J(2) + (U_K + U_S)k_K a_K(2)}{(U_J + U_S)k_J a_J(1) + (U_K + U_S)k_K a_K(1)} -$$

$$\frac{RT}{F}\tau\ln\frac{U_{JS}K_{JS}k_J a_J(2) + U_{KS}K_{KS}k_K a_K(2)}{U_{JS}K_{JS}k_J a_J(1) + U_{KS}K_{KS}k_K a_K(1)} \tag{96}$$

THE TECHNOLOGY OF ION-SELECTIVE ELECTRODES

The classification of ion-selective electrodes

In the field of electrochemical membranes, there has been an extensive and steadily growing interest in the structure and properties of biological membranes, and especially in membranes as a medium for the transport of ions and molecules. During the last six years, attention has been directed to *ion-selective electrodes*. Ion-selective electrodes have certain undisputed advantages: they do not affect the solution studied, are portable, are suitable either for direct determinations or as sensors in titrations, and they are not overly expensive. By the term *specificity* (as distinguished from *selectivity*), is understood the fact that the membrane potential can be affected by only one particular ion in solution. We speak of *selectivity* when the membrane potential can be affected by several ions, among which, however, the electrode selectively favours a certain kind of ion.

Ion-selective electrodes are classified according to the physical state of the substances forming the electrode membrane, or possibly according to the nature of the substances effecting the ion exchange in the membrane[160,562,611]:

I. *Ion-selective electrodes with solid membranes.* In the electrode membrane, a net of a certain kind of ion is formed, the structure of which is constant in time. The membrane can either be homogeneous[160] (a single crystal, a crystalline substance, or a glass which is considered to be a solid with regard to the immobility of the anionic groups), or heterogeneous[118,518], where a crystalline substance is built into a matrix, made, *e.g.*, from a suitable polymer.

II. *Ion-selective electrodes with liquid membranes.* In this case, the electrode membrane is represented by a water-immiscible liquid, in which is dissolved a substance capable of exchanging the ion in solution for which the electrode is selective. This substance is either an associate of this ion with an oppositely charged ion, soluble in the membrane, or it is a complex of the ion, for which the electrode is selective, with an uncharged macrocyclic compound.

This classification is probably the most convenient, especially from the theoretical point of view. It is not expedient to classify ion-selective electrodes according to the homogeneity or heterogeneity of the membrane, etc.

The potential of the ion-selective electrode

1. *The experimental arrangement of the ion-selective electrode*

The ion-selective electrode consists of a membrane, which is generally in contact on one side with a solution containing the ions for which the electrode is selective, and a suitable reference electrode. An example is the lanthanum fluoride ion-selective electrode, which is sensitive to fluoride ions (see Fig. 4). One of the possible arrangements is shown in the scheme

$$\mathrm{Hg}|\mathrm{HgCl_2}|\text{sat. KCl}\|\underset{\Delta\varphi_{\mathrm{L}}(1)}{\text{solution 1}}\left|\begin{matrix}\mathrm{LaF_3}\\ \text{membrane}\end{matrix}\right|0.1\ M\ \mathrm{NaF};\ 0.1\ M\ \mathrm{NaCl}|\mathrm{AgCl}|\mathrm{Ag} \qquad \text{(I)}$$

Another arrangement with a saturated calomel electrode as reference is given by

$$\mathrm{Hg}|\mathrm{Hg_2Cl_2}|\text{sat.KCl}\|\underset{\Delta\varphi_{\mathrm{L}}(1)}{\text{solution 1}}\left|\begin{matrix}\mathrm{LaF_3}\\ \text{membrane}\end{matrix}\right|\underset{\Delta\varphi_{\mathrm{L}}(2)}{0.1\ M\ \mathrm{NaF}\|\text{sat.KCl}}|\mathrm{Hg_2Cl_2}|\mathrm{Hg} \qquad \text{(II)}$$

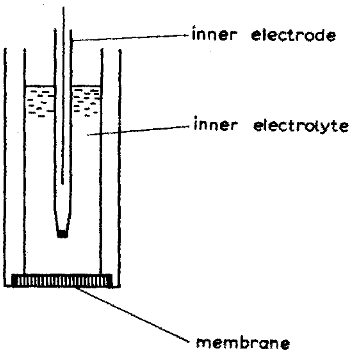


Fig. 4. A diagram of an ion selective electrode with a solid membrane.

The electromotive force of cell (I) is given by the relation

$$E = E_{\mathrm{AgCl/Ag}} + \Delta\varphi_{\mathrm{M}} + \Delta\varphi_{\mathrm{L}}(1) - E_{\mathrm{Hg_2Cl_2/Hg}}(sat.\ \mathrm{KCl}) \tag{97}$$

and that of cell (II) by

$$E = E_{\mathrm{Hg_2Cl_2/Hg}}(sat.\ \mathrm{KCl}) + \Delta\varphi_{\mathrm{L}}(2) + \Delta\varphi_{\mathrm{M}} + \Delta\varphi_{\mathrm{L}}(1) - E_{\mathrm{Hg_2Cl_2/Hg}}(sat.\ \mathrm{KCl}). \tag{98}$$

As will be shown on p. 370, the value of $\Delta\varphi_{\mathrm{M}}$ for the lanthanum fluoride electrode depends on the activity of fluoride and hydroxyl ions, approximately according to eqns. (61) and (62):

$$\Delta\varphi_{\mathrm{M}} = (RT/F)\ln\frac{a_{\mathrm{F^-}}(2) + K^{\mathrm{Pot}}_{\mathrm{F^-,OH^-}}\,a_{\mathrm{OH^-}}(2)}{a_{\mathrm{F^-}}(1) + K^{\mathrm{Pot}}_{\mathrm{F^-,OH^-}}\,a_{\mathrm{OH}}(1)} \tag{99}$$

The sign of $\Delta\varphi_{\mathrm{M}}$ is opposite to that in eqn. (61) since the electrode is anion-sensitive. Equations (97) and (98) have the following important consequence. If the composition of solution 1 is varied, the change in E depends solely on values related to this solution (*i.e.* it is a function of $a_{\mathrm{F^-}}(1) + K^{\mathrm{Pot}}_{\mathrm{F^-,OH^-}}\,a_{\mathrm{OH^-}}(1)$ and of $\Delta\varphi_{\mathrm{L}}(1)$) but it does not depend on values related to solution 2 (the internal solution of the ion selective electrode) or to the internal reference electrode. To avoid determining all values related to its internal composition for each ion-selective electrode independently, these values are comprised in a single constant, E_0, in the case of cell (I)

$$E_0(\mathrm{I}) = E_{\mathrm{AgCl/Ag}} + (RT/F)\ln\left[a_{\mathrm{F^-}}(2) + K^{\mathrm{Pot}}_{\mathrm{F^-,OH^-}}\,a_{\mathrm{OH^-}}(2)\right] \tag{100}$$

and in the case of cell (II)

$$E_0(\mathrm{II}) = E_{\mathrm{Hg_2Cl_2/Hg}}(sat.\ \mathrm{KCl}) + \Delta\varphi_{\mathrm{L}}(2) + (RT/F)\ln\left[a_{\mathrm{F^-}}(2) + K^{\mathrm{Pot}}_{\mathrm{F^-,OH^-}}\,a_{\mathrm{OH^-}}(2)\right] \tag{101}$$

The value of constant E_0, which is different for each electrode, is determined experimentally for the given electrode by calibration with a suitably chosen solution 1. It must be pointed out that the value of E_0 changes with time with certain electrodes, sometimes quite uniformly (the electrode potential drift—see p. 360).

As the ion-selective electrode potential, the following value is defined in this case (and analogously in other cases)

$$E_{\mathrm{ISE}} = E_0 - (RT/F)\ln[a_{\mathrm{F}^-} + K^{\mathrm{Pot}}_{\mathrm{F}^-,\mathrm{OH}^-}\, a_{\mathrm{OH}^-}] \tag{102}$$

It is useful to write schemes (I) and (II) with due regard to the fact that the whole complex of the ion-selective electrode can be denoted as a single electrode, *e.g.*

$\mathrm{Hg|Hg_2Cl_2}$|sat. KCl||solution 1|lanthanum fluoride ion selective electrode

The electromotive force of cell (III) will thus be

$$E = E_0 - (RT/F)\ \ln\ [a_{\mathrm{F}^-}\ (1) + K^{\mathrm{Pot}}_{\mathrm{F}^-,\mathrm{OH}^-}\, a_{\mathrm{OH}^-}] + \Delta\varphi_{\mathrm{L}}(1) - E_{\mathrm{Hg_2Cl_2/Hg}}\ (sat.\ \mathrm{KCl}) \tag{103}$$

In this equation, activity coefficients of individual ions appear, the definition of which requires certain conventions (see p. 354 *et seq.*).

The arrangement of the ion-selective electrode with an internal electrolyte and a reference electrode is not the only possible one. Many years ago, several authors[46,332,647] attempted to replace the internal solution and the internal reference electrode of the glass electrode by a metallic contact. Glass electrodes which have a metal plated internal wall, onto which a metallic connection is soldered, do yield Nernstian response to the hydrogen ion.

A relatively simple situation exists in the case of ion selective electrodes based on silver halides, if the internal contact is made of silver (see ref. 673; similar electrodes are produced by the firm Coleman[104,668]). Kolthoff and Sanders[324] showed earlier that the system

$\mathrm{Ag|AgCl|KCl}\ (c_1)\mathrm{|AgCl|KCl}\ (c_2)\mathrm{|AgCl|Ag}$,

where a cast disk made of AgCl served as a silver chloride membrane, has the same properties as the system in which the membrane is replaced by two electrodes of the second kind connected together

$\mathrm{Ag|AgCl|KCl}\ (c_1)\mathrm{|AgCl|Ag{-}Ag|AgCl|KCl}\ (c_2)\mathrm{|AgCl|Ag}$

The only difference they found was that the membrane electrode has a greater resistance to oxidation. This type of electrode with an internal contact will then behave in the same manner as an electrode of the second kind.

Somewhat more complicated is the lanthanum fluoride ion selective electrode with a vacuum-plated layer of silver or gold[673]. In this case the phases have not a common charge carrier (in the $\mathrm{LaF_3}$ phase this is fluoride ion, and in the metallic phase, electrons), so that the equilibrium between the two phases is not sufficiently well defined. There has not been much experience with this system. Hirata *et al.*[268-271] recommend electrodes with membranes made from the sintered sulphides of heavy metals, with a metallic contact soldered in place.

A similar situation is found with the "Selectrode"[566,567], where the surface of a hydrophobized graphite phase is impregnated with a silver halide mixed with silver sulphide. This mixture represents the electrode "membrane". The name "Selectrode" is, however, now a registered trade mark of the firm Radiometer for all the types of ion-selective electrodes which it produces[373].

An attempt to determine the "standard potential" of precipitate-containing ion-selective electrodes[378] is complicated by the mercury–silver halide, AgX, contact in the authors' cell

Pt|Hg|AgX-membrane|KX (*c*)|AgX|Ag

The different behaviour of this ion-selective electrode from the corresponding electrode of the second kind is probably caused by an interaction between mercury and particles of the silver halide precipitate.

In the case of electrodes with liquid membranes which are in direct contact with an electrical conductor, the nature of the electrode potential of this internal electrode, which is not well defined, represents a complicating factor. Among these electrodes belong one of the modifications of liquid membrane ion-selective electrodes, where the membrane is in contact with a silver plate[499], the "liquid-state electrodes", where a graphite electrode is covered with a film of a solvent immiscible with water and containing either a dissolved complex or a suspension[565,569–571], and, finally, the "coated wire electrode"[90], where a platinum wire is coated with PVC containing an ion exchanger solution (*e.g.* 0.1 *M* calcium-didecylphosphate in dioctyl phosphonate).

2. *The conventional scale of ion activities*

If an unambiguous precise value could be attributed to the liquid junction potential and if reference electrodes had an exactly reproducible value (which condition is not always fulfilled, see refs. 119, 295), it would be possible to determine precisely the individual activity values for series of standard solutions. However, this obviously cannot be done exactly and thus it is necessary to use various approximations or modifications in the measured systems.

The simplest case exists when the studied solution contains an indifferent electrolyte, to whose components the electrode is not sensitive and which has a substantially higher concentration than that of the other ions present in solution 1. Then the activity coefficients of the ions for which the electrode is sensitive— in this case, fluoride and hydroxide—depend solely on the indifferent electrolyte concentration, and not on the concentrations of the fluoride and hydroxide ions (*cf.* ref. 327, p. 35). The liquid junction potential, $\Delta\varphi_L(1)$, also depends practically only on the indifferent electrolyte concentration in solution 1. Equation (103) can then be modified to give

$$\begin{aligned} E = E_0 - (RT/F)\ln\gamma_{F^-} + \Delta\varphi_L(1) - E_{Hg_2Cl_2/Hg}(sat.\ \mathrm{KCl}) \\ - (RT/F)\ln\left\{[F^-] + K^{\mathrm{Pot}}_{(c)\,F^-,OH^-}[OH^-]\right\} \end{aligned} \tag{104}$$

where

$$K^{\mathrm{Pot}}_{(c)\,F^-,OH^-} = K^{\mathrm{Pot}}_{F^-,OH^-}\gamma_{OH^-}/\gamma_{F^-}$$

is the ion selectivity constant, related to a certain composition of the *indifferent electrolyte.* The first four terms on the right-hand side represent a constant, at a given indifferent electrolyte concentration, which can be determined, for a given ion selective electrode, by calibration with a solution containing a fluoride ion concentration such that

$$[\mathrm{F}^-] \gg K^{\mathrm{Pot}}_{(c)\,\mathrm{F}^-,\mathrm{OH}^-}[\mathrm{OH}^-]\,.$$

Of course, the lanthanum fluoride electrode is given here as a simplified example, since in reality the selectivity constant is also a function of the fluoride ion concentration itself (see p. 370).

Equation (102) or (103) is frequently used even in cases where the solution does not contain an excess of indifferent electrolyte, but, of course, the concentration data obtained are subject to errors caused by variations in activity coefficients and the liquid junction potential. At least a partial solution of the problem of indivual activities is provided by the method of conventional activity scales[31-33,383]. This procedure was first used by Bates and Guggenheim[34] when formulating an operational definition of pH (see *e.g.* ref. 327, p. 207, 208), on the basis of which the National Bureau of Standards of the USA worked out a method for determining conventional hydrogen ion activities[32]. The basic assumption of this method is that one can use the Debye–Hückel relation for the individual activity of the chloride ion, in the form[223]

$$-\log(\gamma_{\mathrm{Cl}^-})^0 = AI^{\frac{1}{2}}/(1+1.5\,I^{\frac{1}{2}}) \tag{105}$$

where $A = 0.512\ \mathrm{mol}^{-\frac{1}{2}}\ \mathrm{kg}^{\frac{1}{2}}$ and I is the ionic strength. This assumption was also used by Bates and Alfenaar[33] for the calculation of individual ion activities in solutions suitable for calibration of ion-selective electrodes. Since individual ion activities and mean activities of salts must be mutually consistent, *i.e.* for a salt $\mathrm{A}_n\mathrm{B}_m$ it must hold that (see *e.g.* ref. 327, p. 5)

$$(a_{\mathrm{A}^{m+}}\, a_{\mathrm{B}^{n-}})^{1/(m+n)} = a_{\pm}(\mathrm{A}_n\mathrm{B}_m) \tag{106}$$

it is easy to calculate individual activity coefficients by means of known mean activities. First, on the basis of eqn. (105), cation activities are calculated from the mean activities of their chlorides. Then activities of further anions can be calculated in the same way, by using the mean activities of their salts with the cations whose individual activities have already been determined.

However, eqn. (105) fails at higher ionic strength values. A more precise procedure is based on the Robinson–Stokes equation for the mean molal activity coefficient[35,626a],

$$\ln \gamma_+ = |z_+ z_-| \ln f_{\mathrm{DH}} - \frac{h}{\nu}\ln a_{\mathrm{w}} - \ln[1+0.018(\nu-h)m] \tag{107}$$

where z_+ and z_- are the charges of the cation and anion, respectively, h is the hydration number of the total electrolyte, ν is the number of ions resulting from the dissociation of one electrolyte molecule, a_{w} is the solvent (water) activity, m is the solution molality, and the Debye–Hückel term, f_{DH}, is given by the relation

$$\ln f_{\mathrm{DH}} = -AI^{\frac{1}{2}}/(1+Ba\,I^{\frac{1}{2}}) \tag{108}$$

where A and B are the constants from the Debye–Hückel theory, and a is the ion size parameter. This equation applies up to molalities of $12/h$.

It can be assumed in the case of chloride solutions that the chloride ion is unhydrated, so that a simple relation[35] follows from eqn. (107)

$$\begin{aligned} \ln \gamma_+ &= \log \gamma_\pm + 0.00782\ hm\ g_{\mathrm{m}} \\ \ln \gamma_{\mathrm{Cl}^-} &= \log \gamma_\pm - 0.00782\ hm\ g_{\mathrm{m}} \end{aligned} \tag{109}$$

where m is the solution molality and g_m is the osmotic coefficient of the electrolyte (see *e.g.* ref. 327, pp. 7, 31).

Individual activity coefficients, calculated by means of eqn. (108), which are suitable for calibration of ion-selective electrodes selective for chloride ions[35] or for ions of alkali metals and alkaline earths, are given in Tables II and III.

TABLE II

SINGLE ION ACTIVITY COEFFICIENTS (MOLAL SCALE) FOR UNI-UNIVALENT CHLORIDES AT 25° DERIVED FROM HYDRATION THEORY[35]

m	γ_+	γ_-	γ_+	γ_-	m	γ_+	γ_-	γ_+	γ_-
	HCl		*LiCl*			*NaCl*		*KCl*	
0.1	0.807	0.785	0.799	0.781	0.1	0.783	0.773	0.773	0.768
0.2	0.788	0.746	0.775	0.739	0.2	0.744	0.726	0.722	0.714
0.5	0.812	0.706	0.786	0.695	0.5	0.701	0.661	0.659	0.639
1.0	0.940	0.697	0.882	0.680	1.0	0.697	0.620	0.623	0.586
2.0	1.421	0.717	1.233	0.688	2.0	0.756	0.590	0.610	0.538
3.0	2.357	0.735	1.893	0.706	3.0	0.870	0.586	0.626	0.517
					4.0	1.038	0.591	0.659	0.506
					5.0	1.272	0.600		
					6.0	1.594	0.610		
	RbCl		*CsCl*			*NH_4Cl*			
0.1	0.766	0.762	0.756	0.756	0.1	0.772	0.768		
0.2	0.712	0.706	0.694	0.694	0.2	0.722	0.714		
0.5	0.640	0.628	0.606	0.606	0.5	0.657	0.641		
1.0	0.594	0.572	0.544	0.544	1.0	0.619	0.588		
2.0	0.568	0.525	0.496	0.496	2.0	0.601	0.541		
3.0	0.569	0.505	0.479	0.479	3.0	0.608	0.518		
4.0	0.584	0.496	0.474	0.474	4.0	0.624	0.502		
5.0	0.606	0.492	0.475	0.475	5.0	0.645	0.490		
					6.0	0.667	0.477		

TABLE III

SINGLE ION ACTIVITY COEFFICIENTS (MOLAL SCALE) FOR ALKALINE EARTH CHLORIDES AT 25° DERIVED FROM HYDRATION THEORY[35]

m	γ_{2+}	γ_-	γ_{2+}	γ_-	m	γ_{2+}	γ_-	γ_{2+}	γ_-
	$MgCl_2$		*$CaCl_2$*			*$SrCl_2$*		*$BaCl_2$*	
0.0333	—	—	0.378	0.784	0.1	0.266	0.717	0.259	0.712
0.1	0.279	0.726	0.269	0.719	0.2	0.218	0.681	0.204	0.668
0.2	0.239	0.697	0.224	0.685	0.5	0.190	0.653	0.165	0.630
0.5	0.234	0.688	0.204	0.665	1.0	0.226	0.667	0.167	0.620
1.0	0.344	0.732	0.263	0.690	1.8	—	—	0.229	0.642
2.0	1.439	0.898	0.768	0.804	2.0	0.542	0.753	—	—

TABLE IV

SINGLE ION ACTIVITY COEFFICIENTS OF POTASSIUM AND FLUORIDE IONS IN SOLUTIONS OF POTASSIUM FLUORIDE[558]

(Standard values of pF ($-\log a_{F^-}$). Temperature, 25°)

m (mol kg^{-1})	c (mol l^{-1})	$\gamma_\pm = \gamma_{K^+} = \gamma_{F^-}$	pF
0.01	0.009970	0.903	2.044
0.05	0.04983	0.820	1.387
0.1	0.09961	0.775	1.111
0.2	0.1990	0.727	0.837
0.5	0.4961	0.670	0.475
1.0	0.9868	0.645	0.190
2.0	1.951	0.658	−0.119
3.0	2.888	0.705	−0.325
4.0	3.794	0.779	−0.494

For fluoride-selective electrode calibration, sodium fluoride solutions are inconvenient, especially at higher concentrations ($>0.1\ M$), since marked association occurs[33]. On the other hand, association does not occur with the substantially more soluble potassium fluoride; moreover the hydration numbers of the potassium and fluoride ions are approximately the same ($h_+ \approx h_- = 1.9$); therefore the expression:

$$\gamma_{K^+} = \gamma_{F^-} = \gamma_\pm \tag{110}$$

is valid[558]. The activity coefficient values, together with the value $\text{pF} = -\log a_{F^-}$, are given in Table IV; the a_{F^-} value is the activity on the molal scale.

With the help of electrolyte solutions, whose individual ion activities are tabulated in Tables II, III, and IV, ion-selective electrodes can be calibrated in cells of type III, on the basis of eqn. (103), of course for $K^{\text{Pot}}_{F^-,OH^-}\, a_{OH^-} \approx 0$. By this procedure, the *whole cell* III is actually calibrated. The activity determination of the estimated ion in an unknown solution X, in this case the fluoride ion, is then carried out with the help of the equation[33]:

$$\text{pF}(x) = \text{pF}(s) + \frac{(E_x - E_s)F}{2.303\,RT} \tag{111}$$

where the symbol x denotes the unknown solution and symbol s the standard solution. The condition for the use of eqn. (111) is that the liquid junction potentials in solution x and in solution s differ only by a very small amount.

When this condition is not met, a correction must be made for the change in the liquid junction potential, most simply by using the Henderson equation (43), or possibly the Lewis–Sargent equation (44). Let us denote by the symbol $\delta\Delta\varphi_L$ the difference

$$\delta\Delta\varphi_L = \Delta\varphi_L(x) - \Delta\varphi_L(s) \tag{112}$$

where $\Delta\varphi_L(x)$ and $\Delta\varphi_L(s)$ denote the calculated values of the liquid junction potentials. Then eqn. (111) should be modified to give the form

$$\text{pF}(x) = \text{pF}(s) + \frac{(E_x - E_s - \delta\Delta\varphi_L)F}{2.303\,RT} \tag{113}$$

Measurement of mean activity coefficients in sodium fluoride solutions and in NaF–NaCl mixtures with ion selective electrodes was carried out by Butler[82,84], who used the following cells

$$\begin{array}{l|c|l} \text{glass electrode} & & \text{LaF}_3 \\ \text{selective for Na}^+ & \text{Na}^+, \text{F}^-, \text{H}_2\text{O} & \ \text{electrode} \end{array} \qquad \text{(IV)}$$

and

$$\text{Ag, AgCl}\left|\text{Na}^+, \text{Cl}^-, \text{F}^-, \text{H}_2\text{O}\right|\begin{array}{l}\text{LaF}_3\\ \text{electrode}\end{array} \qquad \text{(V)}$$

He analyzed the results, in the case of cell (IV), using the Harned rule (see ref. 81). Similar studies from the point of view of determination of individual activity coefficients were carried out by Leyendekkers[350] with a cell similar to cell (V), but with a liquid-membrane electrode selective for the chloride ion. Leyendekkers and Whitfield[351,352] studied analogous systems containing alkaline earths ions.

Selectivity

1. *The selectivity constant (coefficient)*

In the previous paragraphs, only the potentials of electrodes selective for at most two univalent ions were discussed, so that it was usually possible to use the following equation for the electrode potential:

$$E_{\text{ISE}} = E_0 \pm (RT/F) \ln(a_1 + K_{12}^{\text{Pot}} a_2) \qquad (114)$$

where the positive sign applies for an electrode selective for cations and the negative sign for one selective for anions.

Equation (114) can be generalized for the case of selectivity for s kinds of ions, carrying charges z_i (always of the same sign).

$$E_{\text{ISE}} = E_0 \pm \frac{RT}{F} \ln \left(a_1 + \sum_{i=2}^{s} K_{1i}^{\text{Pot}} a_i^{1/|z_i|}\right) \qquad (115)$$

where the + sign holds for cation selective electrodes, and the − sign for anion selective electrodes.

There are frequent objections to the term "selectivity constant" (see *e.g.* ref. 402a) and the terms "selectivity ratio" and "selectivity coefficient" are recommended, since this particular value depends upon conditions in the solution and on the means of its determination. Of course, a similar situation exists for the majority of constants, especially those characterizing rate processes in physical chemistry. Accordingly, there seems to be insufficient reason for rejecting the term "selectivity constant". Further, the concept of selectivity in itself implies that the electrode selects among several kinds of ions; the term "selectivity ratio" would, of course, mean that there is some selectivity *per se*, and not that it is a property for comparison. For this reason, the latter term is not considered to be suitable.

Table V gives a survey of relations of the selectivity constant to various physicochemical parameters, as derived in the theoretical part of this review (partly according to Eisenman[160]). In this Table, P_{AJ} and P_{AK} denote the solubility products of the salts AJ and AK, respectively; U_{J}, U_{K}, U_{S}, U_{JS}, and U_{KS} are the mobilities of the particles, J, K, S, JS and KS, respectively; K_{JK} is the ion-exchange equilibrium con-

TABLE V

RELATION OF THE SELECTIVITY CONSTANT TO VARIOUS PHYSICOCHEMICAL PARAMETERS

Kind of membrane	K_{JK}^{Pot}	*Equation*
Solid membrane		
Ions J and K do not transport a charge through the solid phase	P_{AJ}/P_{AK}	(16)
Ions J and K transport a charge through the solid phase	$U_K K_{JK}/U_J$	(62)
Liquid-membrane		
Charged ion exchangers		
Strongly dissociated associates in the membrane	$U_K k_K/(U_J k_J)$	(92)
Negligibly dissociated associates in the membrane	$\frac{U_K+U_S}{U_J+U_S}\cdot\frac{k_K}{k_J}$	
Ion exchanger negligibly mobile ($\tau \to 0$)	$\frac{U_K}{U_J}\cdot\frac{k_K}{k_J}$	(96)
Ion exchanger considerably mobile ($\tau \to 1$)	$U_{KS}K_{KS}/U_{JS}$	
Uncharged ion exchangers	$\frac{K_K}{K_J}$	(72)

stant; R_J and k_K are the distribution coefficients of J and K, respectively; and K_K and K_J are the stability constants of the complexes KS and JS, respectively.

2. *Determination of selectivity constants*

Eisenman, Rudin and Casby[165] proposed that selectivity should be defined as the difference of the ion-selective electrode potentials in solutions of identical concentrations of two ions,

$$E(0.1\ M\ \mathrm{JX}) - E(0.1\ M\ \mathrm{KX}) = (RT/F)\ln K_{JK}^{Pot} \qquad (116)$$

Rechnitz *et al.*[544,545,626] define the selectivity constant as the ratio [J]/[K], when the following equation holds:

$$\Delta E = E(\mathrm{JX}) - E(\mathrm{KX}) = 0 \qquad (117)$$

This procedure has been criticized by Pungor and Tóth[524,525], because, when the electrode is in contact with ion K, ion exchange takes place on the electrode surface and an undefined concentration of ion J is formed at the electrode surface. This, of course, leads to errors in the determination of the selectivity constant. They, therefore, recommend determination of K_{JK} from the dependence of the ion-selective electrode potential on the logarithm of the concentration of ion K, in the presence of a constant concentration of ion J. The dependences obtained are composed of two linear portions (see Fig. 1); at their intercept lies the value $\pm(RT/F)\ln(K_{JK}^{Pot}a_K)$. In Table VI, selectivity constant values[118], which were obtained by the Pungor method[524,515]

TABLE VI

COMPARISON OF SELECTIVITY CONSTANTS OBTAINED BY DIFFERENT METHODS

		Calculated	*Determined by the method of Pungor et al.*	*Determined by the method of Rechnitz et al.*
AgBr electrode;	$K^{\mathrm{Pot}}_{\mathrm{Br^-},\mathrm{Cl^-}}$	$4.9 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$1.0 \cdot 10^{-2}$
AgI electrode;	$K^{\mathrm{Pot}}_{\mathrm{I^-},\mathrm{Br^-}}$	$1.3 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$4.8 \cdot 10^{-3}$

and by that of Rechnitz[544,545], are compared with the values calculated from the solubility products for the silver bromide and silver iodide electrodes (see eqn. 16).

Analytical aspects of ion-selective electrodes

1. *Direct potentiometry*

Direct potentiometry, *i.e.* determination of a substance from a single electrode potential measurement, was used practically only in pH measurements before the appearance of the various kinds of ion-selective electrodes. The indisputable methodological advantage of this approach is, however, complicated in various ways.

A certain complication lies in the fact that the ion-selective electrode does not measure concentration directly, except for solutions containing a constant large excess of an indifferent electrolyte, but the activity of the particular ion in solution which must be recalculated to give the concentration. Of course, this is not always necessary; for, as the pH is a quantitative measure of the acidity of a solution, so the value $\mathrm{pX} = -\log a_{\mathrm{X}}$ describes, often better than concentration, the behaviour of the given ion in solution in its chemical and biological effects. For example, the activity of ionized calcium in serum, as well as the total calcium concentration, are important in biomedical analysis, where the first value can be estimated directly with an ion selective electrode.

The glass electrode is not used for the analytical determination of strong acids or bases at high concentrations, and ion-selective electrodes are similarly of little use in determining particular ions at higher concentrations, since the absolute determination error would be too large.

The relative percentage error in direct potentiometry is given, at 25°, by the equation

$$\%\ \text{error} = 100\ \Delta c_i/c_i \approx 4|z_i|\Delta E \tag{118}$$

where ΔE is the error of the potential measurement in mV and z_i is the charge of the ion to be determined.

In addition to the effect of the liquid junction potential, which has already been discussed, measuring errors can be caused by drift of the E_0 value (see eqn. 100), by long response times, and by temperature effects.

The drift of the E_0 value varies according to the kind of ion-selective electrode. Ross[562] gives a value of 1–2 mV/day so that it is necessary to carry out daily recalibration of the electrode.

The response times of ion-selective electrode have been studied in numerous papers[336,539,541,544–546,653]. The rate of potential stabilization depends on the rate of equilibration or steady-state establishment of the exchange reaction. With ion-selective electrodes made of silver halides, the establishment of the potential proceeds exponentially with time[653], the response time amounts to several tenths of a second and becomes shorter in the presence of an indifferent electrolyte. If the calcium selective electrode is in contact with magnesium ions, a potential "overshoot" first appears, followed by an exponential decrease[544]. The response time of the valinomycin potassium selective electrode depends on the ion concentration[336]; for example, in a solution $10^{-2}\ M$ in K^+, it is about 1 min, while at a concentration below $10^{-4}\ M$, it is 10–15 min. A fast-response differential amplifier[66] has been constructed for measuring rapid potential changes.

The temperature coefficient of the ion-selective electrode[355,356] is a function of the temperature coefficients of both the membrane potential itself and of the reference electrodes, and of the liquid junction potential. An automatic correction is necessary, especially in continuous measurements.

The lower detection limit is in general determined by the solubility of the ion exchanger in the solution studied. The ion-selective electrode potential at too low a concentration of the ion to be determined is not determined by this ion but by the ions formed by dissolution of the ion exchanger[518,521], regardless of whether it is a solid substance, *e.g.* silver halide or lanthanum fluoride, an associate, or a complex dissolved in a liquid membrane. The lower detection limit can be decreased by adding a suitable organic solvent to the solution studied, in order to decrease the solubility product of the sparingly soluble substance forming the membrane of the ion-selective electrode[466].

In analytical applications, the selectivity for a certain ion should be as high as possible, so that the electrode potential exhibits the Nernstian dependence on ion activity within the widest possible activity range. This is fulfilled when K_{1i}^{Pot} is very small for other ions so that, even if they are present in an excess over the ion to be determined, the relationship

$$a_1 \gg K_{1i}^{\mathrm{Pot}}\, a_i^{1/|z_i|} \tag{119}$$

is still valid.

The activity of ions which interfere in the determination of a particular ion, can often be decreased by suitable treatment of the solution. The interference from H_3O^+ and OH^- ion can be eliminated by buffering the solution. In the determination of fluoride, the special buffer, TISAB (see p. 371), simultaneously adjusts the pH of the solution, maintains a constant indifferent electrolyte concentration, and masks several ions which would otherwise form complexes with fluoride ion, thus lowering its activity[188]. Iodide ion, which interferes in chloride determinations with the chloride selective electrode, can be removed by saturating the solution with silver chloride[252].

The accuracy of direct potentiometry can be increased by the standard addition and double standard addition methods[65,147,457,460,464], or by the analate addition method[148].

2. *Other analytical methods*

Titration methods increase considerably[65,518,525] the precision of analytical determinations with ion-selective electrodes, with both precipitation[456] and compleximetric[454] methods. The precision of the determination of the titration endpoint is improved by the use of Gran plots[147,210,211,354]. The firm Orion Research even supplies the graph paper for these plots[462]. A number of papers have been devoted to the theory of titration curves in potentiometric titrations with ion-selective electrodes[12,300,374,583,584]. A convenient titration cell has also been designed[120].

The method of linear null-point potentiometry[146,147] is based on a cell of the type:

$$\mathrm{LaF_3\ electrode}|\mathrm{F^-}\,(c_x),\ \mathrm{KNO_3}(0.1\ M)||\mathrm{F^-}\,(c_s),\ \mathrm{KNO_3}\,(0.1\ M)|\ \mathrm{LaF_3\ electrode}$$

A standard solution containing a suitable concentration of potassium fluoride and 0.1 M potassium nitrate is added to the right-hand compartment of the cell until the electromotive force becomes zero. Then the standard concentration, c_s, equals the unknown concentration, c_x.

Ion-selective electrodes are convenient for ion monitoring, especially in industrial and waste waters[117,145a,355,356,459]; usually it is necessary to employ flow-through methods. These sensors permit relatively high flow rates. When liquid membrane electrodes are used, the flowing liquid must not damage the membrane surface[177].

ION-SELECTIVE ELECTRODES WITH SOLID ION EXCHANGERS

Various membrane materials, which differ in the mechanism of current conductance through the membrane and in the membrane phase structure, belong to this group. Glass electrodes are included in this group, although glass has properties similar to those of a liquid phase. Their common property is that the active centres for the ion exchange within the membrane are fixed and exhibit no mobility. There are two kinds of membranes: homogeneous, composed of a compact active material, and heterogeneous, which contain an active material built into an inactive matrix (silicone rubber, paraffin, etc.).

Silver halide ion-selective electrodes

Silver halides have the character of solid electrolytes, the silver ion acting as the charge carrier (see ref. 323 for silver chloride), which moves through the crystal according to the Frenkel mechanism. The transport process for this mechanism is shown for silver bromide in Fig. 5. Hence, since the current is not transferred by the ion which takes part in the exchange reaction on the membrane surface ($\mathrm{Cl^-}$, $\mathrm{Br^-}$,

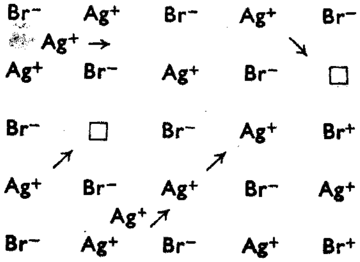


Fig. 5. A scheme for the transport of silver ions in the silver bromide crystal lattice, according to J. I. Frenkel. The silver cations are in interstitial positions in the crystal lattice and the same number of unoccupied lattice positions are in the cation part of the lattice.

I^-), no diffusion potential is formed within the membrane and the membrane potential is given by eqns. (16)–(18).

In practice, there are three typical versions of silver halide membranes. The oldest type, developed by Pungor *et al.*[255,518,522,525] (see also refs. 118, 544, 545)), is a heterogeneous membrane composed of a silver halide precipitate and silicone rubber.

In preparation of the membrane, first a mixture of the precipitate and polysiloxane is homogenized, and then a cross-linking agent (a silane derivative) and a catalyst are added. The final membrane shape is obtained by rolling. The quality of the membrane function depends on the physical nature and quantity of the precipitate incorporated in the membrane, which determine the manner in which the particles are built into the membrane surface. From the cured membrane are then cut circles with a thickness of 0.3–0.5 mm which are fixed onto the end of a glass tube with silicone rubber glue.

Buchanan and Seago[72] recommend mixing of silicone rubber, vulcanized at normal temperatures, with powdered silver halides and pressing it between a polyethylene plate and a polyvinylchloride foil. Electrodes with silver halides precipitates mixed with a thermoplastic polymer[380,668] have proved useful.

Ion-selective electrodes containing silver halides in a silicone rubber matrix are produced by the firm Radelkis[531]; silver chloride, bromide and iodide electrodes are available. According to the pamphlets of this firm, the electrodes require soaking for 1–2 h in a dilute solution of the appropriate potassium halide before use. They can be used at pH values from 2 to 12. The $dE/d\log[X^-]$ value, where E is the electrode membrane potential and $[X^-]$ is the concentration of the halide anion, is about 56 mV. The latest type has a membrane composed partly of silver halide precipitate, built into a silicone rubber matrix, and partly of compact silver halide. For the selectivity constants of these electrodes, see Table VII[525]. These electrodes are suitable for automatic titrations[372].

Electrodes made of silver halides in a polymeric matrix are produced by the firm Coleman[105,106].

Another type of silver halide ion-selective electrode has homogeneous membranes. The "Monokrystaly" Research Institute of Single Crystals in Turnov, Czechoslovakia, which produces CRYTUR electrodes, uses single crystals for silver chloride and silver bromide membranes, and pressed polycrystalline materials for the iodide electrode[686]. Similar materials are used for the AgCl, AgBr, AgI, and AgCN electrodes produced by the firm Philips[493]. This firm also gives the selectivity constants of its electrodes (see Table VIII).

Ross[562] points out that a certain disadvantage of membranes made from compact silver chloride and silver bromide is their large resistance (especially with silver chloride) and formation of photoelectric potentials, so that it is necessary to work in a constant light, which, however, has been questioned[671]. With silver iodide, which conducts electric current well, the membrane material cannot be reliably prepared by casting[562]. For this reason, the firm Orion Research[447] has developed membranes made from a mixture of silver halide with silver sulphide, which is much less soluble than any of the silver halides. Simultaneously it conducts well and serves primarily to increase the membrane conductivity without affecting the membrane potential; the E–$\ln a_{X^-}$ dependences are identical with those of membranes made from pure silver halides.

TABLE VII

THE SELECTIVITY CONSTANTS FOR ION-SELECTIVE ELECTRODES OF THE FIRM RADELKIS (AgCl, AgBr, AgI)[525]

(Selectivity constants were determined by Pungor's method)

Interfering ion, K⁻	K_{JK}^{Pot} *for the electrode made of*		
	AgCl	*AgBr*	*AgI*
CN^-	1	1	1
$S_2O_3^{2-}$	1	1	1
SCN^-	—	0.2	$3\cdot10^{-5}$
Cl^-	—	$6\cdot10^{-3}$	$3.7\cdot10^{-7}$
AsO_4^{3-}	$2\cdot10^{-4}$	$1.6\cdot10^{-6}$	$2.6\cdot10^{-10}$
CrO_4^{2-}		$1.2\cdot10^{-7}$	$6.6\cdot10^{-11}$
CO_3^{2-}	$4.6\cdot10^{-5}$	$1\cdot10^{-7}$	
SO_4^{2-}	10^{-6}	10^{-7}	$1\cdot10^{-7}$
NO_3^-	—	10^{-7}	10^{-8}
SO_3^{2-}	0.2		$5.5\cdot10^{-7}$
PO_4^{3-}	$4.8\cdot10^{-5}$	$3.1\cdot10^{-7}$	$2.5\cdot10^{-11}$
$C_2O_4^{2-}$	$4.5\cdot10^{-5}$		
$Fe(CN)_6^{4-}$			$3.5\cdot10^{-6}$
OH^-			$9\cdot10^{-9}$

TABLE VIII

THE SELECTIVITY CONSTANTS FOR ION-SELECTIVE ELECTRODES OF THE FIRM PHILIPS (AgCl, AgBr, AgI, AgCN)[493]

(Method of determination of selectivity constants unknown)

Interfering ion, K⁻	K_{JK}^{Pot} *for electrodes made of*			
	AgCl	*AgBr*	*AgI*	*AgCN*
Cl^-	—	$6\cdot10^{-3}$	$6.6\cdot10^{-6}$	$2\cdot10^{-5}$
Br^-	1.2	—	$6.5\cdot10^{-5}$	$2\cdot10^{-4}$
I^-	86.5	20	—	3
CN^-	400	25	0.34	—
OH^-	$2.4\cdot10^{-2}$	$1\cdot10^{-3}$	—	—
CO_3^{2-}	$3\cdot10^{-3}$	$2.3\cdot10^{-3}$	$1.2\cdot10^{-4}$	$3.6\cdot10^{-4}$
CrO_4^{2-}	$1.8\cdot10^{-3}$	$1.6\cdot10^{-3}$	$3.7\cdot10^{-3}$	$1.4\cdot10^{-2}$
$S_2O_3^{2-}$	60	1.5	$7.1\cdot10^{-4}$	$2.2\cdot10^{-3}$

Ion-selective electrodes based on silver halides are also produced by the firms Beckman[45], Corning Glass Works[115], Foxboro[180], and Radiometer[533]

Electrodes have also been proposed with membranes applied to hydrophobized graphite, *e.g.* a mixture of silver halide and sulphide[566,567]

The ion-selective electrodes described in this paragraph are suitable chiefly for direct determination of the halide ion concentration in solution (by direct potentiometry), when the halide in the membrane is identical with that in solution. As follows from eqn. (17), an electrode from a less soluble silver halide, X^-, is suitable for determination of another halide, Y^-, which forms a more soluble salt, if the following condition is fulfilled

$$a_{X^-} \ll K^{Pot}_{X^-,Y^-}\, a_{Y^-} \tag{120}$$

This property can be successfully utilized in potentiometric titrations of mixtures of halides with the silver iodide ion-selective electrode. The titration is performed in the presence of barium nitrate, to prevent adsorption of titrant on the precipitate[126].

All three types of silver halide ion-selective electrodes respond to silver ion with a Nernstian slope; however, the silver sulphide ion-selective electrode is more suitable for its determination[525] (see below). The iodide electrode[461] may be used for the determination of mercury(II); however, the slope is not Nernstian[671].

Interferences in the potentiometric determinations with silver halide ion-selective electrodes are sulphide, thiosulphate, and cyanide ions, and reducing media; hence, these electrodes are not suitable for halide determinations in photographic developers. For the effect of the thiocyanate ion on the silver bromide ion-selective electrode, see the paper of Ross[560].

Silver halide ion-selective electrodes can be used in mixtures of alcohol and water, up to about 90% of methanol or ethanol and 40% of *n*-propanol and iso-propanol[310].

As follows from eqn. (29), ion-selective electrodes also respond to anions which dissolve the silver halide solid phase with formation of silver ion complexes. This phenomenon was utilized by Pungor and Tóth[526,654,655] for the determination of cyanide ion with the silver iodide ion-selective electrode. It should be noted that eqn. (29) contains the concentration of free ions of the complexing agent—in this case, the cyanide ion—and this equation cannot be used at pH values where the complexing agent is largely undissociated, or when its ions are bound in another complex. In this case the value, c_Y, represents the total concentration of complexing agent which is not bound in the complex ($c_Y = [Y^-] + [HY]$).

The constant K in eqns. (20) and (27) must then be replaced by the value

$$K' = K \cdot K_{HY}^2/(K_{HY} + [H^+])^2 \tag{121}$$

In the special case, $c_X = 0$, eqn. (27) takes the form

$$K \cdot K_{HY}^2/(K_{HY} + [H^+])^2 = \kappa_X c_X(0)^2/\kappa_{AgY_2}[c_Y - 2(\kappa_X/\kappa_Y)c_X(0)]^2 \tag{122}$$

Hence

$$c_X(0) = c_Y(\kappa_{AgY_2}/\kappa_X)^{\frac{1}{2}} \frac{K^{\frac{1}{2}} K_{HY}/(K_{HY} + [H^+])}{1 + 2(\kappa_X \kappa_{AgY_2}/\kappa_Y^2)^{\frac{1}{2}} K^{\frac{1}{2}} K_{HY}/(K_{HY} + [H^+])^2} \tag{123}$$

In the case when $K_{HY} \ll [H^+]$ and $K^{\frac{1}{2}} K_{HY}/[H^+] \ll 1$, with regard to eqn. (25), the dependence of the membrane potential on pH is expressed by

$$\Delta\varphi_M = (RT/F) \ln c_Y [\kappa_{AgY_2}(\kappa_X)^{\frac{1}{2}} K^{\frac{1}{2}} K_{HY}/([H^+] c'_X)] \approx$$

$$\approx (RT/F) \ln [c_Y (D_{AgY_2}/D_X)^{\beta/2} K^{\frac{1}{2}} K_{HY}/([H^+] c'_X)] \tag{124}$$

Electrodes especially made for determining cyanide ion are supplied by the firms Foxboro[181], Orion Research[447], Philips[493], and „Monokrystaly", the Research Institute of Single Crystals, Turnov (CRYTUR)[629b].

An enzyme ion-selective electrode for amygdalin has also been proposed[361, 550, 550a]. The electrode contains a cyanide solid-state electrode coated with an acrylamide gel containing β-glucosidase. Amygdalin decomposes in the gel and the cyanide ions diffuse to the electrode. The response of this electrode, dE/d log[amygdalin] is about 20 mV, *i.e.* much lower than the Nernstian response.

Various applications of silver halide ion selective electrodes are summarized in Tables IX and X. The silver chloride electrode has also been used for determining

TABLE IX

A SURVEY OF APPLICATION OF SILVER HALIDE ION SELECTIVE ELECTRODES IN INORGANIC ANALYSIS

Use	*Electrode*	*Reference*
^{131}I solution activity	AgI	13
Cl^- in KOH, determination in the presence of Br^- and I^-	AgCl	254
Cl^- in Ca phosphates and halophosphates	AgCl	71, 145
HCl in gaseous mixtures	AgCl	68, 342
Sea water analysis	AgCl	300, 345
I^- in mineral waters	AgI	253, 518
CN^- in waste waters	AgI	525
Cl^- in various materials	AgCl	670
Br^-, $S_2O_3^{2-}$, CN^- in waters (the danger of electrode poisoning)	AgCl, AgBr, AgI	681, 685
Halides in rainfall	AgCl, AgBr, AgI	248
I^- in reacting and equilibrium mixtures	AgI	78, 704, 705
Br^-, SCN^-	AgBr	79

TABLE X

APPLICATIONS OF SILVER HALIDE ELECTRODES IN ORGANIC, BIOLOGICAL, FOOD AND CLINICAL ANALYSIS

Use	*Electrode*	*Reference*
Cl^- in benzoyl chloride hydrolysis	AgCl	62
Determination of tris chloroethyl phosphate	AgCl	125
Cl^- in pharmaceuticals	AgCl	477
CN^- in Sudan grasses	AgI	53
Br^- and I^- in serum	AgBr, AgI	88
CN^- in forage samples	AgI	204
Cl^- in serum	AgCl	129
CN^- in glycosides from fruit and plants	AgI	236
Cl^- in perspiration	AgCl	245, 325
Cl^- in cheese	AgCl	277
I^- in feeds and plants	AgI	278
Cl^- in biological fluids	AgCl	331
Cl^- in plant tissues	AgCl	335
CN^- in plants and alcoholic beverages	AgI	358
Cl^- in milk	AgCl	418, 525
Cl^- at cystic fibrosis	AgCl	440
I^- in biological material	AgI	473, 474

chloride activity within the concentration range, 10^{-5} *M* to 6 *M*[599], and at concentrations of the order of p.p.b.[179].

Electrodes based on silver sulphide

1. *Sulphide ion-selective electrode*

Silver sulphide has two modifications[535]: α-Ag_2S, which is cubic and is an electronic conductor, is stable above 176°, while the modification stable at lower temperatures is monoclinic β-Ag_2S. In this modification at laboratory temperature, silver ions are the major charge carriers[260,562,676], especially if the membrane is in contact with an electrolyte on both sides[178]. The good conductivity and the negligible solubility of the compact membrane ($P_{Ag_2S} = 1.5 \cdot 10^{-51}$)[282] makes the silver sulphide electrode one of the most reliable sensors of this kind.

The silver sulphide ion-selective electrode is produced in two versions. The firm Radelkis supplies the electrode with a membrane made of silver sulphide precipitate built into silicone rubber[523,581]. This electrode requires soaking for 1–2 h in a 0.1 *M* to 10^{-3} *M* solution of silver nitrate before use. A heterogeneous silver sulphide membrane in a thermoplastic matrix was proposed by Mascini and Liberti[381].

A compact membrane, made by pressing polycrystalline Ag_2S[562], is used in electrodes supplied by the firms Beckman[45], Coleman[109], Corning[115], Foxboro[184], Orion Research[447], Philips[494], and "Monokrystaly", the Research Institute of Single Crystals, Turnov (CRYTUR)[629b]. An electrode with silver sulphide precipitated on graphite has also been proposed[571].

These electrodes respond only to sulphide, silver (I) and mercury(II) ions, and to a certain degree, also to cyanide. Theoretically, the slope of the response to sulphide should be Nernstian, $dE/d \log a_{S^{2-}} = 29.6$ mV (at 25°), down to 10^{-19} *M* concentration; however, because of adsorption on the electrode and on the vessel walls, this response is obtained only within the range, 10^{-2} to 10^{-7} *M*, in strongly alkaline sulphide solutions. On the other hand, sulphide activities could be followed down to 10^{-19} *M* values in solutions of HS^- and H_2S[282]. The response to silver(I) exhibits the Nernstian slope, $dE/d \log a_{Ag^+} = 59.1$ mV (at 25°), within the concentration range, 10^{-1}–10^{-7} *M*, if plastic vessels are used instead of glass ones (silver(I) is very strongly adsorbed on glass[82]); see also refs. 147, 282, 358. The free silver(I) activity could be monitored down to the value, 10^{-20} *M*, in silver complexes[562]. The response time is at most several seconds[282].

In addition to acid–base equilibria in solutions containing hydrogen sulphide, Hseu and Rechnitz[282] also followed the equilibrium among solid tin(IV) sulphide, sulphide ion, and thiostannate anion. For other applications of the silver sulphide electrode, see Table XI.

The fact that, in the absence of silver ion in solution, the silver sulphide ion selective electrode shows Nernstian response to mercury(II) ion was utilized by Papp and Havas[476]. Titrations with mercury(II) solutions were used for determination of thiosulphate in the presence of sulphide, for a simultaneous determination of sulphide, thiosulphate and phenylmercaptan, and for determination of polysulphides (after conversion to thiosulphate).

2. *Electrodes containing divalent metal sulphides*

Electrodes provided with a membrane made of a pressed mixture of silver

TABLE XI

APPLICATION OF THE SILVER SULPHIDE ION SELECTIVE ELECTRODE

Substance determined	*Medium or method*	*Reference*
H_2S, sulphides	Atmosphere, waste waters, paper industry	147
Ag^+	Adsorption on glass	149
Sulphides	General study	56, 398
CN^-, Cl^-	Titration with silver (I)	112
Thiol group	Proteins	222, 246
Sulphides	Waste waters	355, 356
Traces of Ag^+	General study	419
S^{2-}	Beer	472
Thiourea	Titration with silver (I)	475

sulphide and sulphides of lead, cadmium, or copper(II) respond to silver ion activity which is affected by the sulphide ion activity, which in turn depends on the activity of the divalent metal in solution[562]. Thus:

$$a^2_{Ag^+} \cdot a_{S^{2-}} = P_{Ag_2S} \tag{125}$$

$$a_{M^{2+}} \cdot a_{S^{2-}} = P_{MS} \tag{126}$$

from which

$$a_{Ag^+} = [(P_{Ag_2S}/P_{MS})a_{M^{2+}}]^{\frac{1}{2}} \tag{127}$$

For the ion-selective electrode potential, the valid expression is:

$$\begin{aligned} E_{ISE} &= \text{const} + (RT/F)\ln a_{Ag^+} \\ &= \text{const} + (RT/2F)\ln(P_{Ag_2S}/P_{MS}) + (RT/2F)\ln a_{M^{2+}} \end{aligned} \tag{128}$$

The electrode is, therefore, selective for the ion M^{2+} in solution, provided that the solubility product of this ion with sulphide ion is substantially larger than the solubility product of silver sulphide. Simultaneously, the MS solubility must be sufficiently smaller than the concentration of the studied ion, M^{2+}, in solution. The exchange reaction between MS and silver sulphide must also be sufficiently fast, a condition which is fulfilled only with certain sulphides. In the acidic region, the sensitivity towards divalent ions decreases because of hydrogen sulphide formation; interference from hydrogen ions is said to be smaller with electrodes based on selenides[270]. The electrode potential shows Nernstian response to the M^{2+} activity within a free ion concentration range of 10^{-1} *M* to 10^{-4} *M* (in the absence of complexes); the lower limit is much smaller in the case of complex equilibria.

Mercury(II) and silver(I) interfere in work with an electrode containing copper(II) sulphide; mercury(II), silver(I) and copper(II) interfere in work with lead sulphide and cadmium sulphide electrodes. A copper(II) sulphide electrode may yield erroneous results when chloride and copper(II) are simultaneously present in the solution. Then the reaction

$$Ag_2S + Cu^{2+} + 2\,Cl^- = 2\,AgCl + CuS$$

may occur. The electrode loses its selectivity towards copper(II) ion and gains sensitivity to chloride ion[562].

Electrodes of this type, selective to lead(II), cadmium(II), and copper(II), are produced by Orion Research[447]; Beckman[45] and Coleman Instruments[107] produce an electrode for copper(II), Corning[115] produces an electrode for lead(II), and "Monokrystaly", the Research Institute of Single Crystals, Turnov, produces an electrode sensitive to copper(II), based on a compact membrane made of a single crystal with the empirical composition[672a], $Cu_{1.8}Se$. This electrode was used for a compleximetric determination of aluminium, based on back-titration with a copper-(II) solution[629a].

Sintered electrodes, based on a mixture of silver sulphide and copper(II) sulphide or lead sulphide, have been proposed by Hirata *et al.*[268,269,271]. Similar electrodes, containing lead selenide or telluride, have also been recommended[270].

The use of electrodes with a silicone rubber membrane containing lead sulphide[266] or copper(II) sulphide[267] has also been considered. Electrodes containing CuS, CdS, or PbS precipitates deposited on the surface of silver sulphide can be used for titrations[11]. An ion-selective electrode sensitive to copper(II) ions, functions very well in determinations of stability constants of copper(II) complexes with various organic ligands[241,539,548,675]. It has also been used in potentiometric titrations (compleximetric titrations with copper(II) as an indicator[379,564], titrations in non-aqueous media[542], titrations of nitrilotriacetic acid[543]). A lead sulphide-containing electrode has served for a $PbSO_4$ association study[198] and for potentiometric titrations of sulphate[563], oxalate[591], and phosphate with lead(II) solution[593]. A cadmium sulphide-containing electrode is suitable for sulphide determination in paper mill liquors[191].

The lanthanum trifluoride electrode

Rare-earth fluorides crystallize either hexagonally (the LaF_3-type lattice), or with formation of rhombic crystals (the YF_3-type lattice). CeF_3, PrF_3, NdF_3, and SmF_2 also have the LaF_3-type lattice. In the lattice of this type, five fluoride ions surround the La^{3+} ion and the six other closest neighbours are again fluoride ions. In total, the lattice is composed of LaF^{2+} layers with a fluoride layer on each wall. Fluoride ions are mobile to a certain degree in this type of lattice[10,207,562,574,579,712].

The ion-selective electrode sensitive to fluoride ion has a membrane made from a lanthanum fluoride single crystal, which has been doped with europium[189]. For electrode preparation, neodymium fluoride and samarium fluoride are also suitable[10,562]. From the point of view of its conductivity, lanthanum fluoride is a solid electrolyte. The conductivity is $10^{-7}\ \Omega^{-1}\ cm^{-1}$ at 27°; fluoride ion is the charge carrier, according to the mechanism[151,608,663].

$$LaF_3 + \text{molecular hole} \rightarrow LaF_2^+ + F^-$$

The solubility product of freshly precipitated lanthanum trifluoride[360] is, at an ionic strength of $I = 0.08\ M$, $P_{LaF_3} = 10^{-17.9}$. Compact lanthanum trifluoride[82] has, however, a lower solubility product, *ca.* $10^{-24.5}$; this value is deduced from the region of the E *vs.* $\log a_{F^-}$ dependence at which the lanthanum fluoride electrode potential ceases to depend on the fluoride ion activity, when it reaches a value corresponding to a saturated lanthanum fluoride solution. A large difference between these solubility products is a rather frequent phenomenon, since it depends on the crystal surface energy, which is much higher with a fresh polycrystalline material than with a single crystal.

The lanthanum fluoride electrode exhibits Nernstian response toward fluoride ion activity, from the neutral region to moderately acidic media, within the fluoride ion concentration range, 1 M to 10^{-5} or 10^{-6} M[82,429,562]. The lower detection limit is 0.02 p.p.m. (*i.e.* about 10^{-6} M) in a solution with an ionic strength of 2, but in pure sodium fluoride it may even be 10^{-7} M[41,44]. Various ions present in solution, affect the electrode potential through changes in the fluoride ion activity (a change in the ionic strength, formation of complexes with the fluoride ion, *e.g.* with aluminium or beryllium ions, formation of HF_2^- ions in an acid medium)[40,57,390]. In these cases, the electrode behaves as an insoluble salt membrane sensitive to a single kind of ion in solution (eqn. 9).

The only important interfering ion is hydroxyl[189], as is shown in Fig. 6[82] for the Orion electrode. The CRYTUR electrode shows a similar potential *vs.* pH dependence. Frant and Ross[189] thought that the selectivity towards hydroxide ions could be characterized by the selectivity constant, $K^{\mathrm{Pot}}_{\mathrm{F^-,OH^-}} = 0.1$; however, it was shown[82] that it varies between zero in 10^{-1} M F^- to a value greater than unity in 10^{-5} M F^-. Moreover, it is time-dependent; the more alkaline the solution, the greater the time-dependence. It is probable that a certain role is played by the hydroxide ion penetrating into the lanthanum fluoride crystal lattice. This process has two consequences: first, a diffusion potential is formed across the membrane (see eqn. (60)); secondly, the freed fluoride ions, diffusing into the solution, affect the membrane potential.

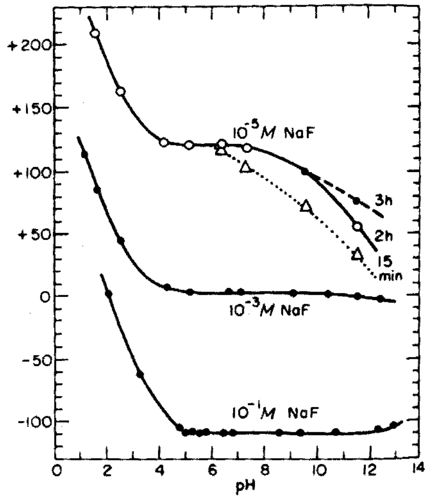


Fig. 6. The effect of pH on the potential of the Orion lanthanum fluoride electrode in sodium fluoride solutions of various concentrations. The potential change with pH in the acidic region is caused by the formation of HF_2^-. (From ref. 82)

Brand and Rechnitz[64] studied the properties of the electric double layer at the lanthanum fluoride membrane–electrolyte interface. The resistance of the lanthanum fluoride single crystal electrodes was studied by Veselý[672].

The stabilization of the electrode potential takes less than 0.5 s at higher fluoride concentrations[623,624]; with good quality electrodes it takes less than 3 min at a 10^{-6} *M* fluoride concentration[528]. The electrodes show a potential drift of about 2 mV per week[359]. Srinivasan and Rechnitz[623] observed a potential change on stirring the electrolyte; this effect appeared in solutions of sodium fluoride alone, at concentrations of less than 10^{-3} *M*, and has so far not been fully explained. The effect is eliminated by the addition of an indifferent electrolyte, which shows the possible electrokinetic nature of the phenomenon.

After prolonged use of the lanthanum fluoride electrode for titrations in solutions containing carboxylic acids (formic, acetic, propionic, *n*-butyric, isobutyric, lactic, malonic, citric and acetylacetic), changes in the electrode surface occur because of the formation of mixed salts of fluoride and an acid anion with the lanthanum ion[9,10]. These changes cause an electrode potential drift, which slowly disappears when the electrode is first immersed in a buffer for a long period of time and is then transferred to a solution of sodium fluoride alone. However, in some cases it is necessary to re-polish the membrane surface.

In order to obtain the desired ionic strength and to adjust the pH of analyzed solutions to 5–5.5, Frant and Ross[188] recommend the addition of the buffer TISAB ("Total Ionic Strength Adjustment Buffer"), containing 0.25 *M* acetic acid, 0.75 *M* sodium acetate, 1.0 *M* sodium chloride, and 10^{-3} *M* sodium citrate. The citrate masks aluminium(III) and iron(III), which would otherwise form complexes with fluoride.

Macdonald and Tóth[366] described an ion-selective electrode based on lanthanum trifluoride built into a silicone rubber membrane. A selective electrode for fluoride, with a bismuth fluoride membrane, has been patented[186].

A systematic study of the direct potentiometric determination of fluoride with the lanthanum fluoride ion selective electrode was carried out by Bock and Strecker[57]. Various modifications of direct potentiometry have been described[146–148,150,151,321,679].

The lanthanum fluoride electrode is suitable as an indicator electrode in potentiometric titrations[8,39,147,185,250,314,354,359,360,444,463,592], and in coulometric titrations[128,420]. These determinations are based on precipitation of fluoride ion with lanthanum(III) or with thorium(IV)[8,359,360] or with tetraphenylarsonium sulphate[302,463]; on complex formation with fluoride ion, *e.g.* with aluminium ion[302,463]; on precipitation of lithium(I) with fluoride in an ethanolic medium[39]; or on precipitation of phosphate with lanthanum(III)[463]. The shape of the potentiometric titration curve is important in precipitation titrations; it is asymmetrical in the vicinity of the equivalence point since the dependence $E = E_1 - (RT/F)\ln a_{\mathrm{F}^-}$ is replaced by the dependence $E = E_2 + (RT/3F)\ln a_{\mathrm{La}^{3+}}$ in this region (which is followed inexactly).

The lanthanum fluoride membrane has been used as a part of a reference electrode for use in certain molten fluorides[70].

Lanthanum fluoride ion selective electrodes are produced by the firms Beckman[45], Coleman[108], Corning Instruments[115], Foxboro[182,183], Orion Research[447], Philips[492], and the Research Institute of Single Crystals, Turnov (CRYTUR)[629b].

The electrodes have been very widely used both for practical analytical purposes (Table XII) and for studies of fluoride complexes (Table XIII).

TABLE XII

THE USE OF THE LANTHANUM FLUORIDE ELECTRODE IN PRACTICAL ANALYSIS

Material analyzed	*Reference*
Inorganic analysis	
Standard method for F^-	44
F^- in fuming nitric acid	122
F^- in chromium plating baths	187
F^- in fluorosilicic acid	305
F^- in baths for regeneration of nuclear fuels	400
F^- in metal oxides	510
F^- in tungsten	528
Raw materials	
F^- in phosphates	71, 145, 153, 170, 612, 660, 662
F^- in minerals and rocks	54, 235, 287, 443, 489, 553, 669, 684, 687
Organic analysis	
Organic substances	3, 185, 281, 357, 480, 595
Explosives	594
Environment	
Air and smoke gases	73, 167, 710
Atmospheric precipitation	248
Drinking and waste waters	19, 111, 123, 124, 154, 249, 303, 355, 356, 386, 478, 555, 571a, 693
Sea water	300, 680
Biology, medicine, and food industry	
Biological materials	27, 168, 307, 312, 385, 425, 559, 637, 683
Bones	26, 613
Teeth	208, 221, 265, 280
Serum	195, 614, 636
Saliva	1, 219
Urine	91, 615, 630, 661
Toothpastes	596
Pharmaceuticals	304a
Foodstuffs and Beverages	650, 173
Plants	73, 347

Glass Electrodes

The glass pH electrode belongs to standard laboratory equipment. Several monographs deal with it, *e.g.* refs. 140, 158, 205, 330, 586.Therefore, only a basic outline of its theory will be given here and only the selectivity of glass electrodes of certain types to alkali metal ions and to silver ions will be treated in greater detail.

The dependence of the membrane potential of thin-walled glass bulbs on the acidity of the solution was observed at the beginning of the present century (see p. 330), but systematic research on the hydrogen response of glass electrodes and the glass composition was not carried out until the late twenties (for a survey see refs. 289, 290). The most significant results were obtained by Hughes[284], and then by MacInnes and Dole[368], who proposed a glass of the composition, 22% Na_2O, 6% CaO, and 72% SiO_2, the production of which was later begun by Corning Glass Works, under the

TABLE XIII

THERMODYNAMIC AND KINETIC APPLICATION OF THE LANTHANUM FLUORIDE ION SELECTIVE ELECTRODE

Problem	*Reference*
HF ionization equilibria	43, 623, 667
AlF_4^- stability constants	43, 624
FeF_4^- stability constants	624
BeF_4^{2-} stability constants	391
SnF_4^{2-} stability constants	243
MgF_3^- stability constants	131, 197
Stability constants of various cations with F^-	18, 59
PbF_2 solubility product	58
Cryolite solubility product	554
Kinetics of formation of FeF_4^- and AlF_4^-	624
Kinetics of aquation of $Co(NH_3)_5F^+$	631
Mechanism of the Fe(III) reaction with I^- in a fluoride medium	625
SF_6 reaction with hydrated electrons	16, 17
Properties of Th^{4+} and U^{4+} complexes with F^-	437

name Corning 015. A similar glass was also prepared by Sokolov and Passynsky[617]. These glass electrodes exhibit Nernstian response to hydrogen ion up to a pH of about 11–12, while deviations depend on the kind and concentration of alkali metal cations present in solution. Sokolov and Passynsky[617] therefore proposed glasses of a similar composition, in which sodium was replaced by lithium or potassium. It was found that a lithium glass shows a negligible deviation from the Nernstian response in 0.1 *M* potassium hydroxide and a small one in 0.1 *M* sodium hydroxide. A glass composed of 14.3% Li_2O, 7% BaO, and 68.7% SiO_2[89], and lithium glasses containing 1–2% mol. Cs_2O and several % mol. La_2O_3 or CeO_2[486] proved to be the best.

The "alkaline error" of the glass electrode is basically caused by the selectivity towards alkali metal ions. This fact led Lengyel and Blum[344] to prepare glasses, mainly based on aluminium silicates and boron silicates, which showed selectivity towards alkali metal ions within a rather wide pH range. The sensitivity of glass to alkali metal ions depends on the presence of trivalent metal oxides in the glass; if their concentration exceeds 10% mol., glass electrodes are obtained which exhibit Nernstian response to 10^{-3}–1 *M* sodium(I) from pH 6 to 10. The selectivity to alkali metal ions was systematically studied by Eisenman *et al.*[165] (see also refs. 611, 649) who proposed the electrode NAS 11–18 for sodium ion determination[115,290], and the electrode NAS 27–06 for potassium ion determination (the numbers denote %mol. of sodium and aluminium). For determination of sodium ion in the presence of potassium ion, glasses can be obtained having $K^{\mathrm{Pot}}_{\mathrm{K^+,Na^+}}$ values up to 250, so that sodium can be determined in the presence of a considerable excess of potassium ion. Unfortunately, the use of glasses with a selectivity to potassium ion, which should contain as much Na_2O as possible, or K_2O as a component, is limited by their durability, which decreases with increasing Na_2O content. It is, therefore, impossible to obtain a usable glass with a $K^{\mathrm{Pot}}_{\mathrm{K^+,Na^+}}$ value smaller than 0.1[115,290]. In Table XIV[540], several types of glasses, together with their selectivity characteristics are given, which, in Rechnitz's[540] opinion, are best for the determination of Li^+, Na^+, K^+,

TABLE XIV

GLASS COMPOSITION FOR GLASS ELECTRODES SUITABLE FOR DETERMINING Li^+, Na^+, K^+, AND Ag^+ [540]

Cation	*Glass composition (in %mol)*	*Selectivity*	*Remark*
Li	15% Li_2O–25% Al_2O_3–60% SiO_2	$K^{\mathrm{Pot}}_{\mathrm{Na^+,Li^+}} \approx 3$, $K^{\mathrm{Pot}}_{\mathrm{K^+,Li}} > 1000$	The best for Li^+ in the presence of H^+ and Na^+
Na	11% Na_2O–18% Al_2O_3– 71% SiO_2	$K^{\mathrm{Pot}}_{\mathrm{K^+,Na^+}} \approx 2800$, pH 11 $K^{\mathrm{Pot}}_{\mathrm{K^+,Na^+}} \approx 300$, pH 7	Nernstian response up to $pNa^+ \approx 5$
Na	10.4% Li_2O–22.6% Al_2O_3–67% SiO_2	$K^{\mathrm{Pot}}_{\mathrm{K^+,Na^+}} \approx 10^5$	Very selective towards Na^+, but a large drift
K^+	27% Na_2O–5% Al_2O_3–68% SiO_2	$K^{\mathrm{Pot}}_{\mathrm{Na^+,K^+}} \approx 20$	Nernstian response up to $pK^+ > 4$
Ag^+	28.8% Na_2O–19.1% Al_2O_3–52.1% SiO_2	$K^{\mathrm{Pot}}_{\mathrm{H^+,Ag^+}} \approx 10^5$	Very Ag^+-sensitive, but unstable
Ag^+	11% Na_2O–18% Al_2O_3–71% SiO_2	$K^{\mathrm{Pot}}_{\mathrm{Na^+,Ag^+}} \approx 1000$	Less Ag^+-sensitive, but more reliable

and Ag^+. Glass electrodes also exhibit a sensitivity towards ammonium ion, which can be determined with suitable potassium-selective electrodes at low concentrations of potassium ion[157].

A remarkable type of glass electrode is represented by systems selective to urea[228,230–233], to amino acids[227,229], and to glutamine[234]. These electrodes consist of an ammonium selective glass electrode, covered with a layer containing a suitable enzyme, which frees ammonium ions from the substance to be determined, the whole being protected by a nylon netting. A disadvantage of these systems is the considerable pH sensitivity of the electrodes.

So far, no glass electrodes showing good selectivity towards divalent cations, especially calcium(II), and sufficient durability, have been prepared[656]; phosphate glasses show a certain selectivity[657].

Glass electrodes selective to a certain kind of alkali metal ions are produced by Beckman[45], Corning Glass Works[115], Electronic Instruments[166], Orion Research [463], Philips[490], Radiometer[534] and others. Special microelectrodes, *e.g.* for subtle measurements inside cells and organs, require a special design (see *e.g.* refs. 193, 265, 317, 318, 405, 590).

Earlier attempts to explain the glass electrode membrane potential, *e.g.* as a Donnan potential with diffusible hydrogen ions, did explain the Nernstian response towards this ion, but could not elucidate the selectivity to alkali metal ions. Nor did these explanations provide a realistic picture of the real mechanism of the membrane potential formation. Hydrogen ion does not penetrate through the membrane at all, as was shown by Schwabe and Dahms[587] using coulometric experiments in which the glass electrode was placed as a cathode in solutions containing tritium. After a 20-h electrolysis, no tritium appeared on the inner side of the glass membrane. The membrane potential formation, however, requires at least slight conductivity of the membrane. Charge is transferred within the membrane by univalent ion transport[304].

The formation of the potential on the glass membrane is caused by ion exchange between the solution and the membrane, as was shown by Schiller[578], Horowitz[279], Dole[139], and Nikolsky[430] (for a survey see ref. 435). The electric potential difference at the solution–glass membrane interface depends on the cation activity ratio—*e.g.* of hydrogen ion—in the solution and in the membrane. The cation activity in the membrane depends on the ion-exchange equilibrium (see eqns. (55)–(57)). The total membrane potential is then given by this expression only when the ion-exchange equilibrium in the membrane is shifted in favour of the cations present in the solution (for example, this situation occurs with glass electrodes made from glass Corning 015, when the solution pH is less than 12). When there are comparable concentrations of at least two cations on the membrane surface, while these concentrations have different values inside the membrane, then, in the case of an equilibrium at the solution–membrane interface, a diffusion potential is formed across the membrane. Equation (61) can be applied[156] to this system.

However, a glass membrane in the electrolyte solution cannot be regarded as a homogeneous system in the direction perpendicular to the membrane surface. Water molecules penetrate the membrane in those places where the membrane is in contact with the solution and form a hydrated layer, about 5–100 nm thick[540]. The formation of this hydrated layer is a condition for good functioning of the glass electrode. The basic character of the glass structure probably does not change in the hydrated layer, but the cation mobility considerably increases compared to the compact inside of the membrane (the univalent cation diffusion coefficient is about $5 \cdot 10^{-11}$ cm^2 s^{-1} in hydrated glass, while in compact glass it is 10^3 times smaller[588]).

The cation transport through the glass[143] has a defect mechanism, where the defect is represented by a cation in an interstitial position. The diffusion coefficient is given by the product

$$D = g < \lambda^2 > f \tag{129}$$

where g is a geometrical factor, λ is the length of the cation jump, and f is the jump frequency, which is given by the relation

$$f = P\,N \tag{130}$$

where P is a value characterizing the probability of the jump and N is the number of cations in interstitial positions. This value depends on the Gibbs energy of the formation of an interstitial cation–vacancy pair, ΔG_f, according to the relation

$$N = p^{\frac{1}{2}} \exp(-\Delta G_f/2RT) \tag{131}$$

where p is the number of possible interstitial positions for one cation. For the value, P, the valid expression is:

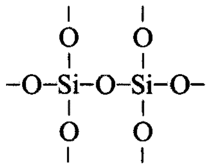
$$P = \nu \exp(-\Delta G_m/RT) \tag{132}$$

where ν is the vibration frequency of the diffusing cation ($\nu \approx 10^{13}$ s^{-1}) and ΔG_m is the Gibbs free energy for transfer of the ion from one interstitial position to another. For judging the effect of structural factors (cation radius, effective radius of the oxygen ion in the glass), the ΔG_f value is most important; according to the Madelung equation, it is inversely proportional to the sum of the cation radius and the effective oxygen ion radius. The value is, therefore, the greater (and the ion mobility smaller), the smaller the cation radius and the effective oxygen ion radius, *i.e.* the closer they can approach each other.

A theory of bi-layer glass membranes, characterized by various ion-exchange constants and various mobilities of the ions being exchanged, has been worked out by Conti and Eisenman[113]. In the stationary state, eqn. (61) or eqn. (55) follow from it, supplemented by a term which is a function of the cation concentrations at the interface between the two membrane phases and of their mobilities, and which can be considered constant during measurements with the glass electrode.

Eisenman[159,162] verified his relation for the selectivity constant (eqn. (63)), using a glass electrode selective to potassium and sodium ions. He first determined $K^{\mathrm{Pot}}_{\mathrm{Na}^+,\mathrm{K}^+} = K_{\mathrm{Na}^+,\mathrm{K}^+}(U_{\mathrm{K}^+}/U_{\mathrm{Na}^+})$ from the dependence of the glass electrode potential on the ratio of the concentrations of the ions. Then he determined the $U_{\mathrm{K}^+}/U_{\mathrm{Na}^+}$ ratio using the diffusion of labelled ions of one kind into the electrode, whose hydrated layer was completely saturated by the other ion by keeping the electrode for a prolonged period of time in a solution of the carbonate of this ion. Finally, he determined the exchange constant for the ions, $K_{\mathrm{Na}^+,\mathrm{K}^+}$, using the diffusion of labelled K^+ into an electrode saturated with Na^+, at various values of the $[\mathrm{K}^+]/[\mathrm{Na}^+]$ ratio in the solution. The calculated and experimental values of $K^{\mathrm{Pot}}_{\mathrm{Na}^+,\mathrm{K}^+}$ agreed relatively well. The sodium ion is roughly ten times more mobile in hydrated glass than the potassium ion.

The selectivity of glass toward alkali metal ions is connected with the effect of the presence of trivalent metal oxides on the glass structure. According to Zachariasen[711], silicate glass has a so-called random network, where each silicon atom lies at the centre of a tetrahedron formed by oxygen atoms. The arrangement of the tetrahedra is not, however, regular, as it would be in a crystal. The oxygen atoms, connecting the silicon atoms, are called bridging oxygens.



$$\begin{array}{ccccc} & | & & | & \\ & \mathrm{O} & & \mathrm{O} & \\ & | & & | & \\ -\mathrm{O}- & \mathrm{Si} & -\mathrm{O}- & \mathrm{Si} & -\mathrm{O}- \\ & | & & | & \\ & \mathrm{O} & & \mathrm{O} & \\ & | & & | & \end{array}$$

In places where there is a univalent cation, M^+, a "non-bridging" negatively charged oxygen is formed. In the presence of an alkaline earth cation, two non-bridging oxygens are formed. Silicon can then be replaced in the cross-linking by aluminium, but the excessive negative charge of the AlO_4^- group must be neutralized, *e.g.* by an alkali metal cation.

The selectivity constant for ion K compared to ion J depends on the ion-exchange constant, K_{KJ}. This constant is given by the ratio of the stability constants of the associates of the given ions with an active site in the ion exchanger, X:

$$K_{\mathrm{KJ}} = K_{\mathrm{JX}}/K_{\mathrm{KX}}\,. \tag{133}$$

The problem can be considerably simplified by assuming the active sites to be one group, while, *e.g.* 6 to 8 AlO_4^- groups are bound to sodium and 8 of them to potassium. According to Williams[498,694], a relation can be found between the associate stability and the ratio of the Pauling radii of the cation and the negatively charged associating anion (*e.g.* a complexing agent) by the following procedure, which was also chosen by Eisenman[156,160,161]: The association of the hydrated ion, KS, with reagent X

$$KS + X = KX + S$$

is accompanied by a change in the Gibbs energy, ΔG_K. This process can be divided into two steps, in which the gaseous ion K(g) takes part:

$$K(g) + S = KS \text{ (Gibbs energy change} = \Delta G_1)$$

$$K(g) + X = KX \text{ (Gibbs energy change} = \Delta G_2)$$

It holds for ΔG_K that

$$\Delta G_K = \Delta G_2 - \Delta G_1 \tag{134}$$

The complex is formed only if $\Delta G_K < 0$. For ΔG_1 can be written, according to the modified Born equation (see *e.g.* ref. 327, p. 10)

$$\Delta G_1 = -A/(r_K + 0.85) = -A/r_{eff} \tag{135}$$

where r_K is the Pauling cation radius and A is a function of the cation charge and the dielectric constant of the medium. For ΔG_2 we can write

$$\Delta G_2 = -B/(r_K + r_X) \tag{136}$$

Here, r_X is the Pauling radius of X, which must be greater than 0.85 Å; B is proportional to the absolute value of the product of the charges of K and X. Figure 7 shows the dependence of ΔG_2 and ΔG_1 on the reciprocal of the effective ion radius, r_{eff}, for the case when a complex is formed. As can be seen, for curve 1, the associate stability decreases with increasing radius of X, while, in the case of curve 2, with increasing radius of X, its stability first increases and then decreases. It can be seen that, with a high electric field strength of X (a small r_X or a large charge on X), the associate stability (and thus also the selectivity towards a number of cations, with respect to a

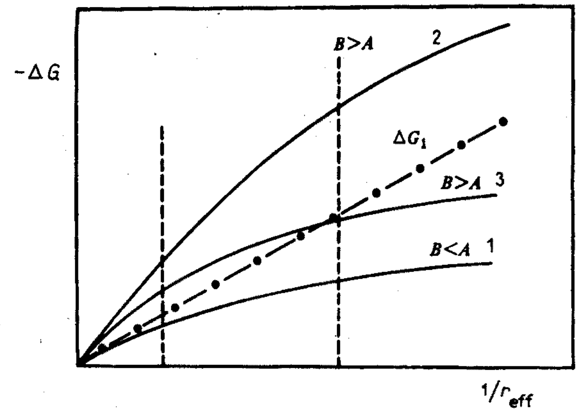


Fig. 7. The Gibbs energy for the formation of a hydrated cation from a gaseous cation (ΔG_1) and for the formation of three complexes (curves 1, 2, 3) from gaseous cations and ligands of various types. (1) A complex with the hydrated cation will not be formed; (2) the ligand is an anion with a large charge or a small size; (3) the ligand is an anion with a small charge or a large size. The real values of r_{eff} correspond to the region between the dashed straight lines. (From Williams [695].)

particular cation) depends linearly on the radius, r_K, *i.e.* the selectivity for lithium ions will be the greatest in the series of the alkali metals. This is true of the classical sodium–calcium glasses, where the non-bridging oxygens represent sites with a strong electric field (the selectivity for the alkali metal ions is, of course, substantially outweighed by the selectivity for H^+). However, with aluminium silicate glasses, the strength of the active-centre field is weakened and various orders of selectivity may occur in the alkali metal series. In this way, it can be qualitatively explained *e.g.* why, with certain glass compositions, the glass electrode is more selective for K^+ than for Na^+ or Rb^+, etc. Eisenman's attempt[161] to treat these considerations quantitatively in a larger number of selectivity series, which are determined by assumed changes in the intensity of the active site electric field, is based on a number of simplifications.

Nikolsky *et al.*[431–435] developed a theory of the electric potential at the membrane–electrolyte interface for the case of an exchange equilibrium between cations in solution and variously active sites in the membrane. In this way they managed to explain, among other things, the origin of an inflection point on the dependence of the glass electrode potential on the pH for some lithium silicate glasses with a small amount of Al_2O_3, Ga_2O_3, or B_2O_3. However, no complete theory of membrane potentials has been formulated so far, which would also take into account diffusion potential formation in the glass, on the Nikolsky assumption of the exchange equilibrium with participation of variously active sites in the membrane.

Other electrode materials with fixed ion-exchange centres

One would think that ion-exchanger membranes based on artificial polymers with ion-exchanging properties would represent a promising solution to the problem of ion-selective electrodes. Surprisingly enough, attempts to obtain such ion-selective electrodes usable for the determination of H^+, Na^+, K^+, Ca^{2+}, Zn^{2+}, Ni^{2+}, SO_4^{2-}, Cl^-, OH^-[23,29,30,61,215–218,242,306,481,519,520,527,708,709] have not yielded successful results in practice.

Precipitate electrodes have found a limited use. Calcium-selective electrodes have been based on calcium oxalate[638] or calcium stearate[639], built into paraffin, and sulphate-selective electrodes, on barium sulphate in paraffin[175,481] or in silicone rubber[519,520,549]. Phosphate-selective electrodes have been based on bismuth phosphate[549] or iron(III) phosphate[225] in silicone rubber, but these electrodes do not seem to be of practical value. A cesium(I)-selective electrode has also been proposed, based on Cs-12-molybdophosphate in silicone rubber[100,101] and a nitrate selective electrode[138], based on a coordination polymer of phenol and formaldehyde containing ammonia and nickel nitrate.

LIQUID MEMBRANES

Ionized ion exchangers

1. *General properties*

Ion-selective electrodes of this kind are based on liquid membranes, in which are dissolved electroneutral salts of the ion studied and of the ion-exchanger ion. The membrane is formed by a layer of a solvent which does not dissolve in the test solution. Various means of fixing the membrane between the test solution and the reference electrode solution are shown in Figs. 8 and 9. As the material for the mem-

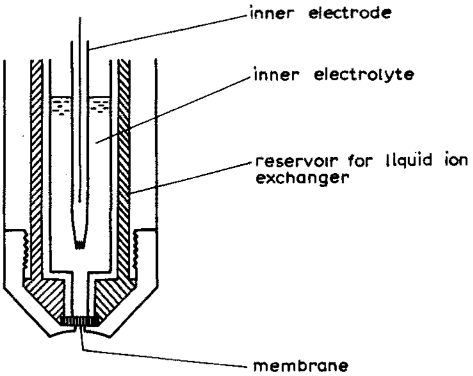


Fig. 8. A liquid membrane ion selective electrode, of the construction used by Orion Research[562].

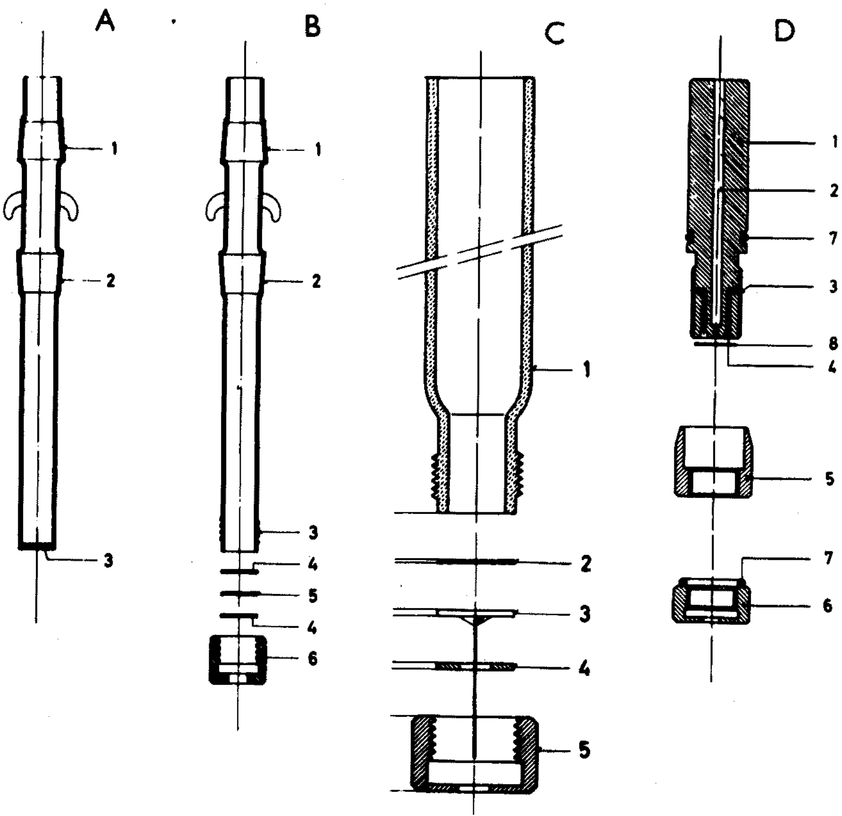


Fig. 9. Various types of liquid membrane ion-selective electrodes[499].

(A) An electrode with a sintered glass filter: (1,2) ground-glass joints; (3) sintered glass filter.

(B) An electrode with a foil membrane: (1,2) ground-glass joints; (3) glass thread; (4) rubber rings; (5) the membrane; (6) the Teflon seal.

(C) An electrode with a silver plate: (1) threaded glass tube; (2) polyethylene ring; (3) silver plate with a soldered-on lead; (4) rubber ring; (5) Teflon seal.

(D) An electrode with a foil membrane, continuously saturated with a liquid ion exchanger: (1) plastic rod (delrin); (2) cylindrical cavity; (3) opening for injecting the ion exchanger; (4) ring ion-exchanger reservoir; (5) plastic ring (delrin); (6) plastic seal (delrin); (7) fixing ring; (8) membrane.

brane skeleton, Orion Research uses a porous flexible plastic membrane; the Corning Glass Laboratories use a sintered glass filter. Pioda[499] tried a sintered glass filter (thickness, 2 mm), porous teflon (MF—Millipore filter; thickness, 150 μm), a filtering textile, Dacron No. 50 (Riwosa A.G., Zurich; thickness, 180 μm), porous polyvinylchloride, Porvic S (Porous Plastics Ltd; thickness, 1 mm), and a filter made from glass fibres (Schleicher and Schuell A.G.; thickness, 200 μm). Dacron and Porvic were not suitable and difficulties with the glass fibre filter were caused by its low mechanical strength. A coated wire electrode[99] (see p. 354) also proved to be useful. An electrode with a liquid ion exchanger fixed in a PVC matrix has also been proposed[402].

In this group are also included electrodes which are sometimes classified as solid ion-exchange electrodes, and which are based, *e.g.* on the calcium salt of dioctylphosphoric acid dissolved in an alcohol–ether solution of collodion. The system formed is then left to dry[541,585]. Ion-selective electrodes from the firm Beckman, are based on a similar principle.

The solvent with which the membrane is saturated must be quite insoluble in water; it must have a low vapour pressure, and must have a sufficiently high viscosity, so that it does not pass through the membrane skeleton quickly. It must allow considerable association of ions in the membrane. A suitable solvent will thus have a low dielectric constant and a rather high molecular weight. Further, it must be available in sufficiently pure form at a reasonable price, and should be light-stable[562].

The liquid ion exchanger must be sufficiently soluble in the membrane and must not dissolve in water. This condition is fulfilled, for example, by substances with long hydrocarbon chains in their molecules. Sufficient selectivity towards the ion, whose activity is to be monitored by the electrode, requires a high stability of the corresponding complex[562] which is influenced, among other things, by the solvent.

The theory of ion-selective electrodes developed by Eisenman *et al.* (see p. 348) is a considerable simplification of the situation in a real liquid membrane. A steady state, which is required by the theory, is usually not attained during measurement; on the contrary, convection occurs when the membrane is in contact with the test solution, and this, in turn, is not taken into account by the theory. The selectivity constants measured thus represent only rough estimations which, however, usually suffice for evaluation of the suitability of the electrode or measurement in the given system (see Table XV).

2. *The calcium electrode*[561]

This ion-selective electrode, whose membrane is a solution of calcium dialkyl phosphate (the alkyl group has an 8–10 membered carbon chain) in dioctylphenylphosphonate[562], exhibits Nernstian response with a slope of 29 mV (at 25°) to the calcium ion within the concentration range 10^{-1}–10^{-5} M. The electrode shows a significant hydrogen ion sensitivity and consequently is usable only within the pH range 6–11. The useful range of the electrode is also limited by the presence of sodium ions, to which the electrode is also sensitive[688]. Currents passing through this electrode on polarization with slow triangular pulses were investigated by Gavach[201].

These electrodes are produced by Beckman[45], Corning Scientific Instruments[115], Orion Research[447], and Philips[496]. This type of electrode has a considerably greater selectivity for calcium ion than for magnesium ions. In some cases, *e.g.*

TABLE XV

THE SELECTIVITY CONSTANTS FOR LIQUID ION-EXCHANGER ION-SELECTIVE ELECTRODES

Ion studied (X)	*Ion-exchanger ion*	*Solvent*	*Interfering ion*	K_{XY}^{Pot}	*Reference*
Ca^{2+}	$(RO)_2PO_2^-$ $(R=C_8H_{17}$ to $C_{16}H_{33})$	Dioctylphenyl-phosphonate	Zn^{2+}	3.2	562
			Fe^{2+}	0.8	
			Pb^{2+}	0.63	
			Cu^{2+}	0.27	
			Ni^{2+}	0.08	
			Sr^{2+}	0.02	
			Mg^{2+}	0.01	562
				0.018	177
			Ba^{2+}	0.01	562
			H^+	10^7	
			Li^+	0.156	177
			Na^+	$1.6 \cdot 10^{-3}$	562
			K^+	0.006	177
			$(CH_3)_4N^+$	0.0067	177
			$(C_2H_5)_4N^+$	0.0051	
			$(C_3H_7)_4N^+$	2.72	
			$C_6H_5(CH_3)_3N^+$	$5.7 \cdot 10^3$	
NO_3^-	Ni (*o*-phen)$_3^{2+}$ [a]	Not given	ClO_4^-	10^3	511, 562
			I^-	20	
			ClO_3^-	2	
			Br^-	0.9	
			S^{2-}	0.57	
			NO_2^-	$6 \cdot 10^{-2}$	
			CN^-	$2 \cdot 10^{-2}$	
			HCO_3^-	$2 \cdot 10^{-2}$	
			Cl^-	$6 \cdot 10^{-3}$	
			CH_3COO^-	$6 \cdot 10^{-3}$	
			$S_2O_3^{2-}$	$6 \cdot 10^{-3}$	
			SO_3^{2-}	$6 \cdot 10^{-3}$	
			F^-	$9 \cdot 10^{-4}$	
			SO_4^{2-}	$6 \cdot 10^{-4}$	
			$H_2PO_4^-$	$3 \cdot 10^{-4}$	
			PO_4^{3-}	$3 \cdot 10^{-4}$	
			HPO_4^{2-}	$8 \cdot 10^{-5}$	
NO_3^-	Methyltricapryl-ammonium ion (Aliquat 336S)	1-Decanol	Cl^-	0.23	102, 103
			SO_4^{2-}	$4 \cdot 10^{-3}$	
			ClO_3^-	0.9	
			NO_2^-	0.5	
ClO_4^-	Fe (*o*-phen)$_3^{2+}$	Not given	OH^-	1.0	562
			I^-	$1.2 \cdot 10^{-2}$	
			F^-	$2.5 \cdot 10^{-4}$	
			NO_3^-	$1.5 \cdot 10^{-3}$	
			Cl^-	$2.2 \cdot 10^{-4}$	
			Br^-	$5.6 \cdot 10^{-4}$	
			SO_4^{2-}	$1.6 \cdot 10^{-4}$	
			CH_3COO^-	$5.1 \cdot 10^{-4}$	

(*Continued on p.* 382)

TABLE XV (*continued*)

Ion studied (*X*)	*Ion-exchanger ion*	*Solvent*	*Interfering ion*	K_{XY}^{pot}	*Reference*
ClO_4^-	Methyltricapryl-ammonium ion (Aliquat 336S)	1-Decanol	Cl^-	$8 \cdot 10^{-3}$	102, 103
			NO_3^-	3	
			SO_4^{2-}	10^{-2}	
			ClO_3^-	0.16	
			PO_4^{3-}	$5 \cdot 10^{-3}$	
			p-Toluyl-sulphonate	0.56	
Cl^-	Distearyldimethyl-ammonium ion	Not given	ClO_4^-	32	562
			I^-	17	
			NO_3^-	4.2	
			Br^-	1.6	
			OH^-	1.0	
			CH_3COO^-	0.32	
			HCO_3^-	0.19	
			SO_4^{2-}	0.14	
			F^-	0.10	
Cl^-	Methyltricapryl-ammonium ion (Aliquat 336S)	1-Decanol	NO_3^-	2.2	102, 103
			SO_4^{2-}	$4 \cdot 10^{-2}$	
			Br^-	3	
BF_4^-	Ni (*o*-phen)$_3^{2+}$	Not given	OH^-	10^{-3}	562
			I^-	20	
			Br^-	$4 \cdot 10^{-2}$	86
			CH_3COO^-	$4 \cdot 10^{-3}$	
			HCO_3^-	$4 \cdot 10^{-3}$	
			F^-	10^{-3}	
			Cl^-	10^{-3}	
			SO_4^{2-}	10^{-3}	
CNS^-	Methyltricapryl-ammonium ion (Aliquat 336S)	1-Decanol	Cl^-	$3 \cdot 10^{-4}$	102, 103
			NO_3^-	$6 \cdot 10^{-2}$	
			SO_4^{2-}	$8 \cdot 10^{-3}$	
			ClO_4^-	0.54	
			I^-	0.28	

[a] Abbreviation *o*-phen denotes *o*-phenanthroline.

in determination of water hardness, this property is not utilized and for this reason Orion Research has developed an electrode with the same ion exchanger which is, however, dissolved in the cheaper solvent, decanol ("the divalent cation electrode"). This liquid membrane has roughly identical selectivities towards calcium and magnesium, and the selectivities for other ions can be found in Table XVI. This electrode is produced by Beckman[45], Corning Scientific Instruments[115], and Orion Research[447].

In the field of physicochemical studies, the calcium ion-selective electrode has

TABLE XVI

THE SELECTIVITY CONSTANTS OF THE "DIVALENT CATION" ELECTRODE WITH A MEMBRANE MADE OF A SOLUTION OF CALCIUM DIALKYLPHOSPHATE IN DECANOL

Interfering ion (Y)	$K^{\mathrm{Pot}}_{\mathrm{Ca/Y}}$	*Reference*	*Interfering ion*	$K^{\mathrm{Pot}}_{\mathrm{Ca/Y}}$	*Reference*
Zn^{2+}	3.5	562	Na^+	0.01	562
Fe^{2+}	3.5	562	Na^+	0.025	177
Cu^{2+}	3.1	562	K^+	0.018	177
Ni^{2+}	1.35	562	$(CH_3)_4N^+$	0.016	177
Ba^{2+}	0.94	562	$(C_2H_5)_4N^+$	0.156	177
Sr^{2+}	0.54	562	$(C_3H_7)_4N^+$	7.40	177
Li^+	0.124	177	$C_6H_5(CH_3)_3N^+$	$1.6 \cdot 10^4$	177

been used for determination of the calcium ion activity coefficient[22,81,82,285,351,352], for determination of the solubility and dissociation of $CaSO_4 \cdot 2H_2O$[424,635] and $CaCO_3$[423] and for determining the stability constants of calcium complexes with tri- and tetrametaphosphate[682] .It has also been used to study equilibria between calcium ions and nitrilotriacetic acid and EDTA[540,546,547] (see also ref. 696); the kinetics of the displacement reaction

$$Ca^{2+} + MgY^{2-} \rightleftharpoons CaY^{2-} + Mg^{2+}$$

where Y^{4-} is the anion of the completely dissociated EDTA were also measured. The same electrode was used by Fleet and Rechnitz[177] in a flow-through apparatus, to measure the rates of the biologically important very fast reactions of calcium ion with lactic, succinic, tartaric, and gluconic acids. To measure reaction rates in similar systems with magnesium ion instead of calcium ion, these authors used the electrode for simultaneous determination of calcium and magnesium ions. This electrode can be converted into a beryllium-selective electrode by treatment with a beryllium ion-containing solution[447]; this electrode has been used[177] to measure the rates of the reactions of beryllium ions with the above acids. The electrode was similarly modified by Moya and Cheng[411], to serve as an indicator electrode for titrations of various di- and trivalent cations with triethylenetetraminehexaacetic acid.

Both the calcium electrode and the "divalent cation" electrode exhibit Nernstian response towards cyclohexylammonium ions[110].

The principles of potentiometric calcium(II) determination with an ion selective electrode have been dealth with in numerous papers[239,320,416,598,634,689–691] (for a review see ref. 147).

A survey of the analytical applications of the calcium-selective electrode in biology, medicine, and the food industry is given in Table XVII. For determination of free calcium ions in biological media, flow-through electrodes must be used[407].

Other analytical studies have involved calcium determination in bentonites[174,388], in soil[707], in sea water[301,645,646], in detergents[127], and the study of $MgSO_4$ and $CaSO_4$ association in sea water[315,316]. The calcium-selective electrode was used to evaluate the chelating properties of detergent builders[54].

A heterogeneous liquid electrode, calcium ion selective, was proposed by

3. *Potassium electrode*

A potassium-selective electrode of unspecified composition, in which tetraphenylborate is the ion exchanger[713], is supplied by the firm Corning[113]. The selectivity towards potassium compared to sodium ($K^{\mathrm{Pot}}_{\mathrm{K^+,Na^+}} = 1.2 \cdot 10^{-2}$) is relatively low. Potassium in serum has been determined with this electrode[703]. Walker *et al.*[115a,677] used an ion-exchanging solution from the firm, Corning, in microelectrodes for measuring the intercellular potassium ion activity (see Fig. 15). With this electrode, the intracellular potassium ion concentration in the luminal fluid of turtle thyroid follicles[96a], in frog sartorius muscle[331a], the extracellular brain potassium concentration during spreading depression and anoxic depolarization[674a], and the work-induced increase of extracellular potassium concentration in muscle[273a], were determined.

TABLE XVII

ANALYTICAL APPLICATIONS OF THE CALCIUM-SELECTIVE ELECTRODE IN BIOLOGY, MEDICINE, AND THE FOOD INDUSTRY

System analyzed	*Reference*
General methods and reviews	15, 353, 404, 405, 407, 557
Serum	14, 49, 251, 406, 445, 446, 505, 506, 529, 530, 536, 556, 573
Blood, brain and spinal fluid	406, 408, 572
Saliva	63, 220
Gastric juices	409
Binding of calcium in organisms	664, 706
Cellular processes	94, 199[a], 487, 488
Milk	328, 417
Animal fodder	5

[a] The authors used the "divalent cation electrode".

Shatkay[55,292,597]. It is based on a thenoyltrifluoroacetone solution in tributylphosphate, which is dispersed in a polyvinylchloride membrane.

4. *Anion electrodes*

In Table XV are given some *o*-phenanthroline complexes, which function as ion exchangers in ion-selective electrodes sensitive to nitrate, perchlorate, and fluoroborate. As can be seen from the Table, their sensitivity towards other anions is not negligible, so that the electrodes are only suitable for analysis of solutions which meet a number of conditions. These electrodes can be used from pH 4 to 7. Ion-selective electrodes for the above-mentioned kinds of ions are produced by Beckman[45], Corning[115], and Orion Research[447].

The use of the nitrate electrode[562] for direct potentiometry was investigated by Potterton and Shults[511]. The lower detection limit was also determined[2]. The electrode was used for the study of the complex formation of lanthanum ions with nitrate ions[322], and as an indicator electrode in the titration of nitrate with diphenylthallium(III) sulphate[135,136]. In practical analysis, the electrode has served for the determination of nitrate in soil extracts[67,370,371,421,442], in vegetables and other plant materials[24,25,370,397,422,479,674,687], in waters[77,313,339,601], in microbial media[375], in limestone[92], in oleum[552], in nitrites[202], and for determining traces of NO_2 and NO in gaseous mixtures[137].

The perchlorate electrode[291,562] has so far been used only as an indicator electrode in the titration of perchlorate with tetraphenylarsonium chloride[21,616], and for determining the solubility product of $KClO_4$, $[Co(NH_3)_6](ClO_4)_3$, $[Cupy_4]$-$(ClO_4)_2$, and $[Fe(o\text{-phen})_3](ClO_4)_2$, where py denotes pyridine and *o*-phen, *o*-phenanthroline[283].

The tetrafluoroborate electrode contains a $[Ni(o\text{-phen})_3](BF_4)_2$ solution in the membrane. It is useful for potentiometric determination of boron after its conversion to tetrafluoroborate[86,87] and as an indicator electrode in the titration of tetrafluoroborate with tetraphenylarsonium chloride[616]. Electrodes selective towards perrhenate[272], picrate[20], and salicylate[259] ions have also been described. Phosphate-selective electrodes based on heteropoly compounds[226] have little significance.

Ion-selective electrodes with a liquid membrane based on the formation of ion pairs of quarternary ammonium cations containing long aliphatic chains with anions have been proposed by Sollner and Shean[603,618,621,622] (see also ref. 60). These membranes are marked by their high selectivity towards the type of ionic charge (they are practically impermeable for other cations), but their selectivities to various anions do not differ very much. As Sollner and Shean[621] point out, they obey the Hofmeister lyophilic series. For this reason the ion-selective electrodes of a similar type for nitrate, perchlorate, chloride and thiocyanate, shown in Table XV, also show poor selectivity. This is also true for electrodes whose membranes contain salts of various amino acids with the methyltrilaurylammonium ion, which are to serve for amino acid analysis[382], and for a tetraalkylammonium ion-sensitive electrode, based on a PVC membrane plasticized with N,N-dimethyloleamide[264].

The firm Corning has developed an acetylcholine-selective electrode[37] (Corning Model 476,200). It was used for determination of choline esterase[36] and for studying the inhibitive effect of organic pesticides on choline esterase[38].

In this group of ion-selective electrodes also belong the so-called "liquid-state" electrodes[568-571], formed by solutions of complexes of various metals with dithizone in *o*-xylene, adhering to a graphite electrode. The selectivity of these electrodes is probably not very high, although the authors state that they were able to measure silver ion activity in solution within the range 10^{-2}–10^{-13} *M*. Similar electrodes, based on PVC plasticized with dipentylphthalate, impregnated with dithizone[338], have also been described.

Liquid membranes with electroneutral carriers

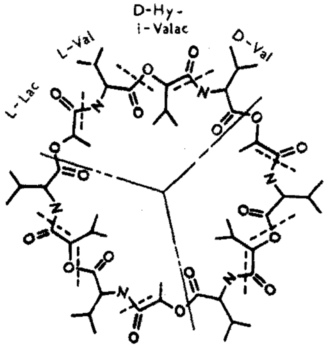
In this section liquid membranes whose ion-exchanging components are dissolved macrocyclic compounds will be discussed. The macrocyclic compounds form complexes, especially with alkali metal ions and with ammonium ion, which show great stability in non-polar solvents, compared to that in water. Since this is a well defined group of substances having considerable importance in biochemistry (they are mostly substances with antibacterial effects), they are dealt with separately.

1. *Macrocyclic substances*

These macrocyclic substances belong among cyclic *depsipeptides* (α-amino acids and α-hydroxyaliphatic acids are alternately bound in a ring), *macrotetrolides* (tetralactone of nonactinic acid and of its derivatives), *polyethers*, and some other substances. The great majority of these substances are electrically uncharged under those acid–base conditions at which their complexing action takes place in artificial and natural membranes; they form 1:1 complexes with the alkali metal ions, which consequently carry a single positive charge. In this context, it is also necessary to mention antibiotics which have an anionic character, but which also make membranes ion selective because of formation of complexes with the alkali metal ions; these are, *e.g.*, nigericin and monensin.

Depsipeptides (for a summary see refs. 468, 471, 604). The most important substance of this group is valinomycin with a 36-membered ring.

It was isolated from *Streptomyces fulvissimus* cultures[69] and is prepared by microbial synthesis according to MacDonald and Slater[365] (for the total synthesis see ref. 605). Studies of valinomycin itself by proton magnetic resonance, infrared spectroscopy, and optical rotatory dispersion[293,469,607] have shown that, in non-polar solvents, all the NH groups form intramolecular hydrogen bridges so that the



Valinomycin

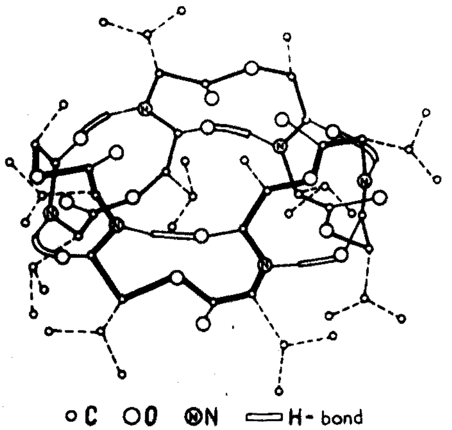


Fig. 10. The valinomycin structure in a non-polar solvent (from refs. 469, 607).

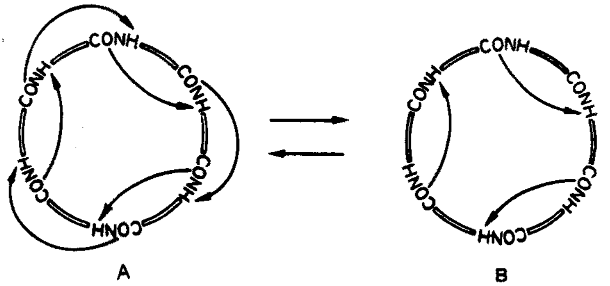


Fig. 11. A diagram of the equilibrium between the internally associated and a less associated valinomycin structure in a solvent of medium polarity (from refs. 469, 607).

molecule assumes the characteristic bracelet structure (see Fig. 10) with a dipole moment of 2.5–1.5 D. In more polar solvents, hydrogen bridges are formed between the NH groups and the solvent molecules, so that both the structures are in equilibrium (see Fig. 11). It is worth mentioning that, because of the preservation of a somewhat polar character even in non-polar solvents, valinomycin is adsorbed on the surface of phospholipid membranes[607].

On complex formation with the alkali metal ions, a pronounced change in the ligand structure occurs[258,293,384,441,469,607] and the characteristic cylindrical structure[498a], with a diameter of 15 Å and a height of 12 Å, is formed (see Fig. 12). Owing to this structural change, all polar groups are directed towards the centre of the molecule, where the alkali metal ion is, while the non-polar lipophilic groups form an outer envelope to the whole structure. This is the cause of the very high solubility and stability of the complex in non-polar solvents, *e.g.* in phospholipid layers of cell membranes, and its considerable instability in aqueous solutions. The large ligand volume and the polar character of the inside of the complex probably prevent ion-

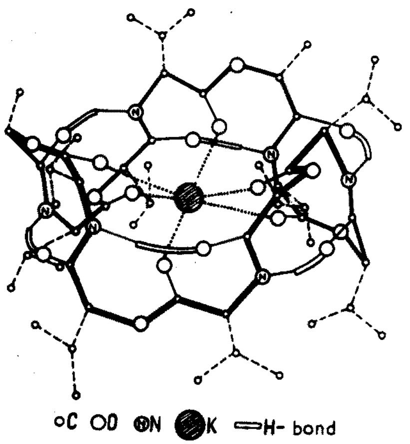
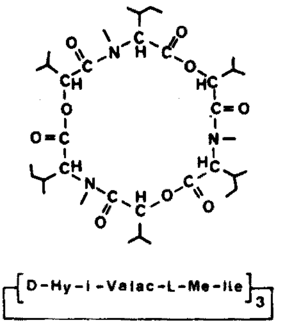


Fig. 12. The structure of the valinomycin complex with potassium ions (from refs. 469, 607).

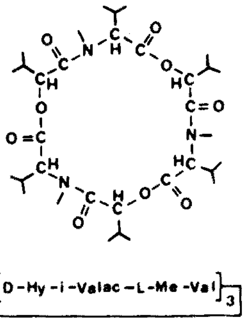
pair formation between the complex and anions in solvents with low dielectric constants.

The remarkable properties of valinomycin are due to the position of particular building units and their conformation. The interchange between D-valine and D-alanine leads to about a 20-fold decrease in the stability constant of the complex with potassium ions, while the antibiotic properties are preserved; the replacement of D-valine with D-leucine, and of L-valine with L-leucine leads to a mere 5-fold decrease in the stability constant, but there is a remarkable decrease of antibacterial properties[607]. If the configuration of a single D-valine is changed, the valinomycin activity for intake of potassium into mitochondria drops to 13%, and on replacing a single L-lactate with the D-configuration, it drops to 2.2%[514]. On inverting the configuration of all building units in the valinomycin molecule, so-called enantio-valinomycin[607] is formed, whose complexing and biological properties are identical with those of valinomycin.

In this group also belong the antibiotic enniatins with 18-membered rings, isolated[509] from cultures of the mould *Fusarium orthoceras*, var. *enniatinum* (for the synthesis see ref. 468), and beauvericin[244].



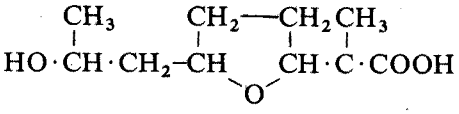
Enniatin A



Enniatin B

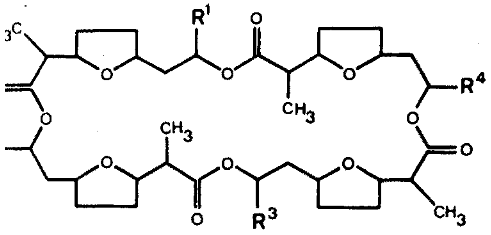
These substances behave similarly to valinomycin, but the stability of their complexes with the alkali metal ions is smaller. Enniatin C has no antibiotic properties[607]. In molecules of the complexes of valinomycin and enniatin B, potassium has the coordination number 8[410].

Macrotetrolides (in the literature the term macrotetralides also appears; the name tetrolides, expressing, according to the Geneva nomenclature, a 4-fold lactone, would actually suffice). This group of antibiotics was discovered by Prelog *et al.*[141] in cultures of various actinomycetes, especially of the variety Streptomyces. They are tetralactones, derived from nonactinic acid,



$$\begin{array}{l}\mathrm{\quad\;\; CH_3 \qquad\quad CH_2\text{—}CH_2\,CH_3}\\ \mathrm{\qquad |\qquad\qquad\quad |\qquad\quad |\quad\;\; |}\\ \mathrm{HO\cdot CH\cdot CH_2\text{–}CH \qquad CH\cdot C\cdot COOH}\\ \mathrm{\qquad\qquad\qquad\qquad\diagdown_{O}\diagup}\end{array}$$

which are substituted in various ways:



$R^1 = R^2 = R^3 = R^4 = CH_3$ Nonactin

$R^1 = R^2 = R^3 = CH_3$ $R^4 = C_2H_5$ Monactin

$R^1 = R^3 = CH_3$ $R^2 = R^4 = C_2H_5$ Dinactin

$R^1 = CH_3$ $R^2 = R^3 = R^4 = C_2H_5$ Trinactin

The macrotetrolide molecules are rather flexible and are able to bind cations with rather different ionic radii. Figure 13 shows the structure of the nonactin complex with potassium ion, obtained on the basis of the X-ray structural analysis[319]. These results were confirmed by investigation of the nonactin complexes of the alkali metal ions using proton magnetic resonance[516,517]. Potassium has the coordination number 8 in the complex.

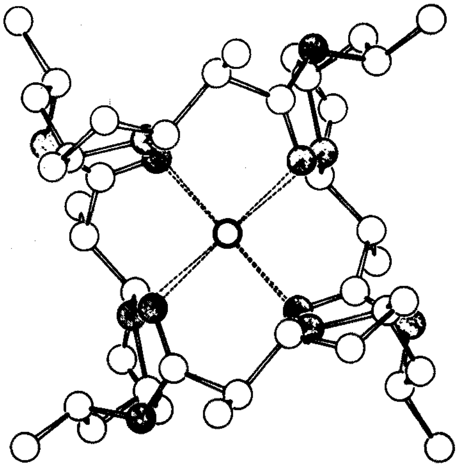
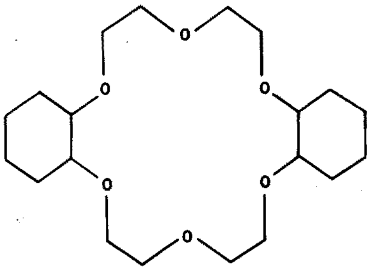


Fig. 13. The structure of the nonactin complex with potassium ions (from refs. 319, 499). (○) Carbon atom, (●) oxygen atom, (O) potassium ion.

Polyethers. So far the most important substance from this group, binding potassium into a more stable complex than the other alkali metals, is 2,3,11,12-dicyclohexyl-1,4,7,10,13,16-hexaoxacyclo-octadecene.



Its discoverer, Pedersen[482], named the substance dicyclohexyl-18-crown-6. The number 18 relates to the number of members in the ring and 6 denotes the number of heterocyclic oxygens. It is prepared by condensation of bis(*o*-hydroxyphenoxy)ethylether with bis (chloroethyl)ether, in the presence of sodium hydroxide. In this way, dibenzo-18-crown-6 is formed, from which dicyclohexyl-18-crown-6 is prepared by catalytic hydrogenation. The discovery was made by chance—during preparation of bis(*o*-hydroxyphenoxy)ethylether by the reaction of bis(chloroethyl) ether with the sodium salt of *o*-hydroxyphenoxytetrahydropyrane[95]. The synthesized substance consists of two isomers, probably the *meso* and *dl* forms[192]. Since the discovery, over 60 different cyclic polyethers have been prepared[95,98,192,483,484]. In view of the importance of these substances, which both function as ion-selective carriers, and can dissolve the alkali metal ions in non-polar solvents[152,482,644a], several reviews have been published[98,485,659].

The complexes are formed by an ion–dipole interaction between the ether oxygen and the central atom. The selectivity order is determined, with crowns having 15–18-membered rings, by the size of the cavity[95,192,483] (see Table XVIII). The question will be discussed in greater detail below. The complexes of the crowns with the above-mentioned number of ring members are roughly planar[80,658]. However, the potassium complex with dibenzo-30-crown-6 consists of a wrap-around structure with all oxygen atoms approximately equidistant from the central ion but not in the same plane[80]. The formation of complexes with the crown-to-univalent metallic ion ratio 2:1 cannot, however, be excluded (they are probably of the "sandwich" type)[192,483]. It has been stated[387] that di-*tert*-butyldicyclohexyl-18-crown-6 forms complexes with a 3:1 ligand-to-metal ratio in phospholipid bilayers. Polymeric macrocyclic substances with ion selective properties of the type of poly(vinylbenzo-15-crown-5) and poly(vinylbenzo-18-crown-6) have also been described[326].

TABLE XVIII

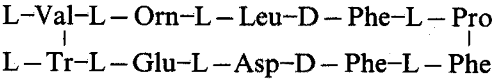
CAVITY SIZES OF POLYETHERS

Polyethers	*Cavity diameter (Å)*
All 14-crown-4	1.2–1.5
All 15-crown-5	1.7–2.2
All 18-crown-6	2.6–3.2
All 21-crown-7	3.4–4.3

Macrocyclic polyethers with heteroatoms in their rings, especially with nitrogen, have been described by Lehn *et al.*[133,134,343]. Some of these show a pronounced selectivity towards strontium compared to barium, but they are probably unsuitable for ion selective electrodes because of their solubility in water. Macrocyclic diamines binding halides into their cavities have also been described[609].

Other substances. A significant selectivity for barium ions[348] is exhibited by the polymer of nonylphenoxypolyoxyethylene glycol (Igepal CO-880).

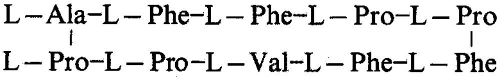
The gramicidins, obtained from filtrates of *Bacillus brevis* cultures[200] are antibiotics with peptide character, which bind alkali ions in complexes. To this group belong cyclic gramicidin S



$$\begin{array}{l}\text{L–Val–L – Orn–L – Leu–D – Phe–L – Pro}\\ \quad\;| \qquad\qquad\qquad\qquad\qquad\qquad\qquad\;\; | \\ \text{L – Tr–L – Glu–L – Asp–D – Phe–L – Phe}\end{array}$$

and acyclic formylpentadecapeptideethanolamines, gramicidins A,B, and C, and the cyclic decapeptide, tyrocidin A.

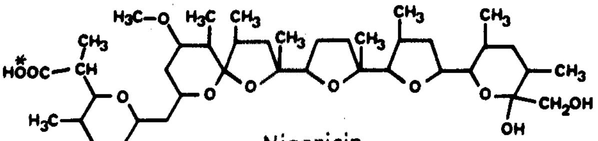
A significant selectivity for sodium compared to potassium is shown by another decapeptide, antamanide[294,692]



$$\begin{array}{l}\text{L – Ala–L – Phe–L – Phe–L – Pro–L – Pro}\\ \quad\;| \qquad\qquad\qquad\qquad\qquad\qquad\qquad\;\; | \\ \text{L – Pro–L – Pro–L – Val–L – Phe–L – Phe}\end{array}$$

Ion selectivity is also shown by an artificially prepared bicyclic peptide[589].

The antibiotics nigericin (polyetherin A) from the culture *Streptomyces hygroscopicus*[245a] and monensin from the culture *Streptomyces cinamonensis*[244a] (as well as grisorixin[196], X-537A and X-206[47]), are present as anions in approximately neutral solutions. Their complexes with the alkali metal ions are thus uncharged particles[499,513,515]. They are included here only because they are structurally similar and because of their close origin to the other substances of this group. X-Ray structural analysis of the silver salts of both the substances[4,334,629] has shown that they form a ring around the alkali metal cation, which binds nigericin through five and monensin through six oxygen atoms. The complexes are sparingly soluble in water.



Nigericin

2. *Complexing and transport properties of macrocyclic substances and their effect on membrane potentials*

Stability constants and selectivity. The stability constants of macrocyclic compounds with the alkali metal ions were determined by conductometry[607], microcalorimetry[194,363], nuclear magnetic resonance[516,517], polarography[327a], potentiometry with cation-specific glass electrodes[192,499,504], spectroscopy[703a], thermometric titration calorimetry[296,297], and vapour pressure osmometry[499,503]. A survey of selected stability constants is given in Table XIX. The stability of the complexes in aqueous solutions is very low and for this reason the values given are mostly for various non-aqueous solvents.

Complex formation with macrocyclic compounds consists predominantly of an interaction between the ion, from which the original solvate envelope has been removed, and the dipoles of the complexing agent. A solvate cavity is thus formed for the ion, similar to that in water; the outer shell of this cavity is, of course, strongly hydrophobic. To explain the pronounced selectivity towards ions of a certain radius, similar considerations can be used as in the case of glass selectivity to a certain alkali metal ion[160,695] (see p. 376 *et seq.*).

The ion selectivity of macrocyclic substances in membranes is, however, determined not only by the complex stability in the membrane but also by the interaction between the ion and the solvent (usually water), which is in contact with the

TABLE XIX

SELECTED STABILITY CONSTANTS OF MACROCYCLIC COMPOUND COMPLEXES WITH THE ALKALI METAL IONS

Macrocyclic compound	*Log (stability constant) for the ion*					*Solvent*	*t(°)*	*Ref.*	*Comments*
	Li^+	*Na^+*	*K^+*	*Rb^+*	*Cs^+*				
Valinomycin		1.08	>390			Methanol	25	499, 700	
		0	6.30	6.41	5.81	Ethanol	25	607	
Enniatin B		2.38	2.92			Methanol	25	499, 700	
		3.11	3.57	3.60	3.34	Ethanol	25	606, 607	
Beauvericin	2.0	2.48	3.49	3.54	3.54	Ethanol		470	
Nonactin		2.58	3.83	3.57	3.15	Methanol	30	410	log K_{BaX} 1.72
		3.30	4.11			Ethanol	30	410	log K_{BaX} 2.40
Monactin		2.58	3.83	3.57	3.15	Methanol	30	410	log K_{BaX} 1.28
		2.54	4.28			Ethanol	30	410	log K_{BaX} 2.43
Dicyclohexyl-18-crown-6 (isomer A)	−0.2	0.2	0.34		0.10	Water	25	192	log $K_{\mathrm{NH_4X}}$ 0.15 log K_{AgX} 0.36 log K_{TlX} 2.4[b] logK_{SrX} 3.2[b] logK_{BaX} 3.5[b]
		4.08	6.01	4.43[a]	4.61	Methanol	25	192	logK_{TlX} 5.20[a]
Dicyclohexyl-18-crown-6 (isomer B)		0.2	0.25	−0.05		Water	25	192	log$K_{\mathrm{NH_4X}}$ −0.1 log K_{AgX} 0.15 log K_{TlX} 1.8[b] log K_{SrX} 2.6[b] log K_{BaX} 3.3[b]
		3.68	5.38		3.49	Methanol	25	192	
Dicyclohexyl-14-crown-4		2.18	1.38			Methanol	25	192	
Cyclohexyl-18-crown-5		3.71	3.58		2.78	Methanol	25	192	
Dibenzo-18-crown-6		4.36	5.00		3.55	Methanol	25	192	
Dibenzo-21-crown-7		2.40	4.30		4.20	Methanol	25	192	
Dibenzo-24-crown-8			3.49		3.78	Methanol	25	192	
Dibenzo-30-crown-10		2.0	4.60			Methanol	25	192	
Dibenzo-60-crown-20			3.90			Methanol	25	192	
Antamanide		3.4	2.4			Ethanol		294	
Nigericin		4.38	5.18			Methanol	25	364	
Monensin		5.85	4.98			Methanol	25	364	

[a] Mixture of isomers (ref. 327a).
[b] From ref. 98.

membrane, *i.e.* the value of the standard Gibbs free energy of cation transfer[410] is given by

$$\Delta G_{\mathrm{C}}^{0} = \Delta G_{\mathrm{L}}^{0} - \Delta G_{\mathrm{H}}^{0} \tag{137}$$

where $\Delta G_{\mathrm{L}}^{0}$ is the standard Gibbs free energy of the ion interaction with the macrocyclic ligand and its surroundings, and $\Delta G_{\mathrm{H}}^{0}$ is the standard Gibbs free energy of cation hydration. For an approximate calculation, Morf and Simon[410] assessed various components of the $\Delta G_{\mathrm{L}}^{0}$ value, namely, the standard Gibbs free energies corresponding to:

i. the interaction between the ion and the *n* dipoles of the ligand, and the interaction among the dipoles of the ligand;

ii. the interaction between the ion and the membrane solvent as a structureless dielectric;

iii. the cavity formation for the complex in the membrane solvent;

iv. the change in the ligand conformation so that the coordinating groups can surround the equilibrium cavity inside the ligand, with the minimum strain in the ligand structure (the value is independent of the ion radius);

v. the ligand deformation so that it just matches the given ion (this value depends on the radius of the ion);

vi. the change in the partial molar volume of the solvent due to the presence of ions.

The cation coordination number, which determines the minimum dimension of the cavity inside the ligand, is of basic importance. The minimum cavity dimension corresponds to the case when the terminal atoms of the coordinating groups, *e.g.* oxygens, touch each other, forming the structure corresponding to the appropriate coordination symmetry. If the ion radius is smaller than the radius of the minimum cavity, then ΔG_L^0 has a constant value and the Gibbs free energy of cation transfer depends only on the Gibbs free energy of hydration, whose absolute value increases with decreasing ion radius.

This consideration allows various series of selectivities to be obtained as functions of ion radii and possibly of ion charges[410]—as has already been done by Eisenman[160] on a simpler model.

As has already been mentioned (p. 346), translocation of ions occurs between the two boundary planes of the liquid membrane, and is manifested in the case of a single ion by mere self-diffusion, without net mass transport. In the case of an exchange equilibrium with several ions, practically no diffusion potential is formed across the membrane, since the mobility of the complexes is practically identical .Thus, in one of the hypotheses concerning transport in the membrane[340,515,651], it is proposed that the complexes, and possibly the complexing agent present in low concentration, are freely mobile in the membrane, and that the macrocyclic substance functions as a carrier[399]. Regarding the high rate of equilibrium establishment between the macrocyclic complex and its components, in the case of the alkali metal ions[132,602], rapid ion exchange takes place between the complexes and the complexing agent (carrier-relay[697,702]). The majority of macrocyclic substances behave in this way[171,329,697-699,701]. Another hypothesis, assuming that the macrocyclic substance forms a transmembrane channel[93,413], is operative solely with peptides, gramicidins[329,665,666].

Macrocyclic compounds in thin natural and artificial membranes. The remarkable properties of macrocyclic compounds of the above types were first observed in their effect on biological processes, especially on oxidative phosphorylation in mitochondria. In a number of papers (*e.g.* refs. 169, 213, 341, 389, 515, 648, 701), the effect of macrocyclic antibiotics as agents uncoupling oxidative phosphorylation has been described, and it was found that this property is ion specific, since it is particularly connected with the presence of potassium ions in the solution in which the mitochondria are placed. Anionic macrocyclic antibiotics of the nigericin type suppress this effect[212,513a]. Simultaneously it was discovered that this effect is connected with the ability of uncharged macrocyclic substances to enable transport of the alkali metal ions through the membranes of mitochondria, in an ion-specific manner[93,172, [212–214,240,247,340,403,512,514,651]. For a theoretical discussion of the problem, see refs. 399, 702.

Membranes of cells and cell organelles are probably formed by a phospholipid bilayer, on each side of which is deposited a protein layer[130]. The membrane thickness lies between 50 and 130 Å. A suitable model for a biological membrane is the so-called black phospholipid film, composed of a phospholipid bilayer (for a review, see *e.g.* ref. 257). Macrocyclic antibiotics enable transport of alkali metal ions through these membranes, as is manifested *e.g.* in a decrease in the membrane electric resistance[6,7,164,209,256,413,414,513,515,652,701]. For example, if the potassium chloride solution on both sides of a phospholipid bilayer membrane containing valinomycin[7] is changed in concentration from $10^{-2}\ M$ to $10^{-1}\ M$, the membrane resistance drops from $5 \cdot 10^5\ \Omega\ \mathrm{cm}^{-2}$ to $6.3 \cdot 10^2\ \Omega\ \mathrm{cm}^{-2}$; the membrane resistance is $2 \cdot 10^8\ \Omega\ \mathrm{cm}^{-2}$ with $10^{-1}\ M$ sodium chloride. The concentration limit of the valinomycin effect in the membrane is as low as $10^{-11}\ M$[209]. A similar ion-specific effect on the potassium ion transport is shown *e.g.* by macrotetrolides, during electric current passage through a liquid membrane of a similar thickness as that in ion selective electrodes[697–699,701].

Membrane potentials are formed, on artificial lipid bilayer membranes in which macrocyclic complexing substances are dissolved[6,164,346,412,415,632,633], as is shown, for example, in Table XX.

As has already been mentioned (p. 348), Ciani, Eisenman, and Szabó[99,632] worked out a theory of membrane potentials for these thin membranes, in which the electroneutrality condition is not observed, and verified it[160,164,632,633] on lecithin bilayer membranes in which was dissolved $10^{-7}\ M$ nonactin or trinactin, or $10^{-4}\ M$ dicyclohexyl-18-crown-6, utilizing the determined ratios of the stability constants for pairs of alkali metals[163].

TABLE XX

THE MEMBRANE POTENTIALS (mV) FORMED ON PHOSPHOLIPID BILAYER FILMS WITH A DISSOLVED MACROCYCLIC CARRIER, SEPARATING SOLUTION (2) $5 \cdot 10^{-2}\ M$ Li AND SOLUTION (1) CONTAINING IONS OF THE OTHER ALKALI METALS IN CONCENTRATIONS OF $5 \cdot 10^{-2}\ M$

(From ref. 412)

Carrier	*Alkali metal ion in solution* (1)			
	Na$^+$	*K*$^+$	*Rb*$^+$	*Cs*$^+$
Valinomycin	8	151	172	135
Enniatin B	0	90		21
Dinactin	5	85	110	35
Gramicidin A	15	60	65	35

3. *Ion-selective electrodes*

Ion selective electrodes utilizing macrocyclic carriers, suitable for determination of the alkali metal ions, are of three kinds.

The first kind of electrode employs simple liquid membranes, as described on p. 378 *et seq.*, and natural macrocyclic compounds. Originally, these ion-selective electrodes were based on nonactin and its homologues[627,628,646] (see Table XXI) but later it was observed that the most advantageous system for potassium determination,

TABLE XXI

THE SELECTIVITY CONSTANTS FOR ION SELECTIVE ELECTRODES WITH MACROCYCLIC CARRIERS

Carrier	*Solvent forming the membrane*	*Ion J*	*Ion K*	K_{JK}^{Pot}	*Ref.*
Valinomycin (0.009 *M*)	Diphenylether	K^+	Li^+	$2.1 \cdot 10^{-4}$	499, 501
			Na^+	$2.6 \cdot 10^{-4}$	
			Rb^+	1.9	
			Cs^+	0.38	
			NH_4^+	$1.2 \cdot 10^{-2}$	
			Mg^{2+}	$1.8 \cdot 10^{-4}$	
			Ca^{2+}	$2.6 \cdot 10^{-4}$	
			H_3O^+	$5.4 \cdot 10^{-5}$	
Nonactin (0.3 *M*)	50% Nujol, 50% 2-octanol		Li^+	$5.6 \cdot 10^{-4}$	499, 500
			Na^+	$6.7 \cdot 10^{-3}$	
			Rb^+	0.42	
			Cs^+	$3.1 \cdot 10^{-2}$	
			NH_4^+	2.5	
			H_3O^+	$1.8 \cdot 10^{-2}$	
Nonactin (0.04 *M*)	Diphenylether		Na^+	10^{-2}	499, 500
Monactin (0.04 *M*)	50% Nujol, 50% 2-octanol		Na^+	$2 \cdot 10^{-2}$	499, 500
Monactin (0.03 *M*)	Diphenylether		Na^+	$8.3 \cdot 10^{-3}$	499, 500
72% Nonactin 28% Monactin (0.3 *M*)	50% Nujol, 50% 2-octanol		Na^+	$3.1 \cdot 10^{-2}$	499, 500
72% Nonactin 28% Monactin (sat. solution)	Tris(2-ethylhexyl) phosphate	NH_4^+	Li^+	$4.2 \cdot 10^{-3}$	582
			Na^+	$2.0 \cdot 10^{-3}$	
			K^+	$1.2 \cdot 10^{-1}$	
			Rb^+	$4.3 \cdot 10^{-2}$	
			Cs^+	$4.8 \cdot 10^{-3}$	
			Ca^{2+}	$1.7 \cdot 10^{-4}$	
			H_3O^+	$1.6 \cdot 10^{-2}$	

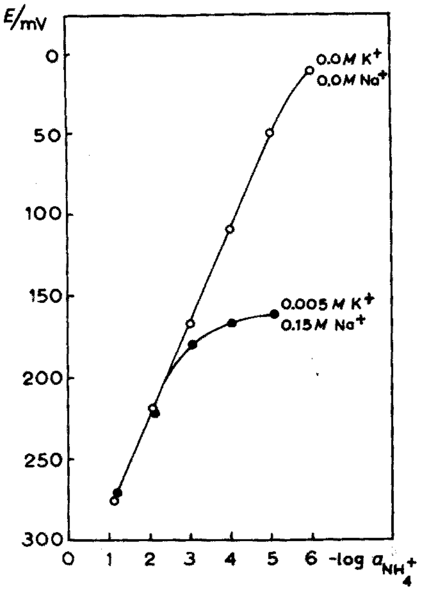
with a high selectivity compared to sodium, is an electrode with a liquid membrane containing a valinomycin solution in diphenylether[500,501,610]. The selectivity constants for this electrode are given in Table XXI. They were also studied in other papers[171,336]. This electrode[499,501] exhibits Nernstian response to potassium ions within the concentration range, 0.1 *M* to 10^{-5} *M*. The membrane resistance is roughly 1 MΩ. The response time has been studied[97,336,501].

This electrode is produced by Orion Research[96,190,447,448,451,458] and Philips[490,497].

The electrode has been used for the determination of potassium in various systems[83,502], and also for determination of the potassium activity during formation of the complex between ATP and potassium ions[401,551].

The significant selectivity of macrotetrolide electrodes towards ammonium ions[503] was utilized in an electrode with a liquid membrane containing a saturated solution of a mixture of macrotetrolides (72% nonactin and 28% monactin in tris-

(2-ethylhexyl)phosphate[582]). It has properties similar to those of the valinomycin electrode, with respect to its resistance and response time (see also ref. 377). The dependence of its potential on the ammonium ion activity is shown in Fig. 14. This electrode is manufactured by Philips[495].



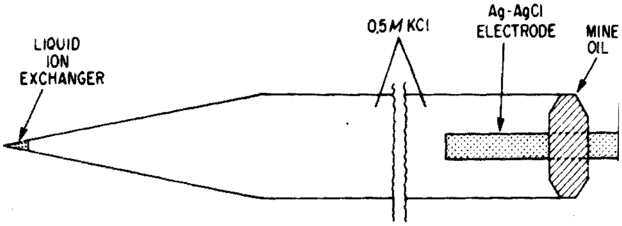


Fig. 14. The dependence of the potential of an ammonium selective electrode on the activity of ammonium ions alone (curve 1) and in the presence of 0.15 M Na^+, 0.005 M K^+, which is the approximate ionic composition of blood serum (curve 2). (From ref. 582).

Fig. 15. The potassium microelectrode as described by Walker[677]. With permission of the American Chemical Society.

Orion Research have attempted the preparation of an ion selective electrode based on polyethers[458]. However, the electrode did not exhibit Nernstian response to potassium ion; the potassium–sodium selectivity constant is $K^{\mathrm{Pot}}_{K^+,Na^+} \approx 0.1$.

Beckman[45] have developed "solid membrane" ion-selective electrodes for determination of potassium[333] and ammonium[116] ions. Since the selectivity constants are close to the values for the valinomycin and the macrotetrolide electrodes (see Table XXI), these electrodes probably employ these macrocyclic carriers built in a suitable matrix. Ion selective electrodes based on a plastic foil, prepared by evaporating a PVC solution in cyclohexanone with addition of a macrocyclic substance in dipentylphthalate, have been proposed by Petránek and Ryba[489a]. The valinomycin electrode has a selectivity and Nernstian response which does not differ from the liquid membrane electrodes; the response is practically instantaneous. Among polyethers, the following proved to be especially advantageous in these membranes: dimethyldicyclohexyl-18-crown-6 ($K^{\mathrm{Pot}}_{K^+,Na^+} = 1.0 \cdot 10^{-2}$) and dipropyldicyclohexyl-18-crown-6 ($K^{\mathrm{Pot}}_{K^+,Na^+} = 1.8 \cdot 10^{-2}$; instantaneous response). These electrodes exhibit Nernstian response to potassium ion within the range, $10^{-1,5}$–10^{-5} M.

The "liquid state" potassium electrode[565] is based on a solution of valinomycin or dicyclohexyl-18-crown-6 in mesitylene.

A barium ion-selective electrode[348] has been prepared by precipitating nonylphenoxypolyoxyethylene glycol (see p. 390) in an aqueous solution containing a barium salt, with tetraphenylborate. The precipitate formed is dissolved in *p*-nitroethylbenzene.

SUMMARY

A review of theory and applications of ion-selective electrodes is presented. After a full discussion of the theoretical background, the general technology of ion selective electrodes is described. Solid-state electrodes, liquid ion-exchanger, and macrocyclic carrier electrodes are then reviewed.

RESUME

Une revue est présentée sur la théorie et les applications des électrodes ioniques sélectives. Après discussion sur le bruit de fond théorique, on décrit la technologie générale de ces électrodes, type: état solide, échangeur liquide ionique et macrocyclique.

ZUSAMMENFASSUNG

Eine Übersicht über Theorie und Anwendungen ionenselektiver Elektroden wird vorgelegt. Nach einer ausführlichen Diskussion der theoretischen Grundlagen wird die Arbeitstechnik mit ionenselektiven Elektroden beschrieben. Festkörperelektroden und Elektroden mit flüssigen Ionenaustauschern und makrocyklischen Trägern werden dann besprochen.

REFERENCES

1 R. Aasenden, F. Brudevold and B. Richardson, *Arch. Oral Biol.*, 13 (1968) 625.
2 W. Abbolt, *J. Miss. Acad. Sci.*, 14 (1968) 11.
3 M. E. Aberlin and C. A. Bunton, *J. Org. Chem.*, 35 (1970) 1825.
4 A. Agtarap, J. W. Chamberlin, M. Pinkerton and L. Steinrauf, *J. Amer. Chem. Soc.*, 89 (1967) 5737.
5 R. D. Allen, J. Hobley and R. Carriere, *J. Ass. Offic. Agr. Chem.*, 51 (1968) 1177.
6 T. E. Andreoli, J. A. Bangham and D. C. Tosteson, *J. Gen. Physiol.*, 50 (1967) 1729.
7 T. E. Andreoli, M. Tieffenberg and D. C. Tosteson, *J. Gen. Physiol.*, 50 (1967) 2527.
8 T. Anfält, D. Dyrssen and D. Jagner, *Anal. Chim. Acta*, 43 (1968) 487.
9 T. Anfält and D. Jagner, *Anal. Chim. Acta*, 47 (1969) 483.
10 T. Anfält and D. Jagner, *Anal. Chim. Acta*, 50 (1970) 23.
11 T. Anfält and D. Jagner, *Anal. Chim. Acta*, 56 (1971) 477.
12 T. Anfält and D. Jagner, *Anal. Chim. Acta*, 57 (1971) 165.
13 H. Arino and H. H. Kramer, *Nucl. Appl.*, 4 (1968) 356.
14 D. E. Arnold, M. J. Stansell and H. H. Malvin, *Amer. J. Clin. Pathol.*, 49 (1969) 52.
15 M. J. Arras, *Postgrad. Med.*, 45 (1969) 52.
16 K. D. Asmus and J. H. Fendler, *J. Phys. Chem.*, 72 (1968) 4285.
17 K. D. Asmus and J. H. Fendler, *J. Phys. Chem.*, 73 (1969) 1583.
18 A. Aziz and S. J. Lyle, *Anal. Chim. Acta*, 47 (1969) 49.
19 R. H. Babcock and K. A. Johnson, *J. Amer. Waterworks Ass.*, 60 (1968) 953.
20 S. G. Back, *Anal. Lett.*, 4 (1971) 793.

21 R. J. Baczuk and R. J. Dubois, *Anal. Chem.*, 40 (1968) 685.
22 J. Bagg, *Aust. J. Chem.*, 22 (1969) 2467.
23 J. Bagg and H. P. Gregor, *J. Amer. Chem. Soc.*, 83 (1961) 3576.
24 A. S. Baker and R. Smith, *J. Agr. Food Chem.*, 17 (1969) 1284.
25 A. S. Baker, N. H. Peck and G. E. MacDonald, *Agron. J.*, 63 (1971) 126.
26 G. Bang, T. Kristoffersen and K. Meyer, *Acta Pathol. Microbiol. Scand.*, A 78 (1970) 49.
27 F. W. Barnes and J. Runcie, *J. Clin. Pathol.*, 21 (1968) 668.
28 F. E. Bartell, *Proc. Nat. Acad. Sci.*, 6 (1920) 308.
29 A. S. Basu, *J. Indian Chem. Soc.*, 35 (1958) 451.
30 A. S. Basu, *J. Indian Chem. Soc.*, 39 (1962) 619.
31 R. G. Bates, *Determination of pH*, New York, 1964, Chap. 3.
32 R. G. Bates, *J. Res. Natl. Bur. Stand.*, A 66 (1962) 179.
33 R. G. Bates and M. Alfenaar, *Activity Standards for Ion-Selective Electrodes*, Chapter 6 of ref. 288.
34 R. G. Bates and E. A. Guggenheim, *Pure Appl. Chem.*, 1 (1960) 163.
35 R. G. Bates, B. R. Staples and R. A. Robinson, *Anal. Chem.*, 42 (1970) 867.
36 G. Baum, *Anal. Biochem.*, 39 (1971) 65.
37 G. Baum, *Anal. Lett.*, 3 (1970) 105.
38 G. Baum and F. B. Ward, *Anal. Chem.*, 43 (1971) 947.
39 E. W. Baumann, *Anal. Chem.*, 40 (1968) 1731.
40 E. W. Baumann, *Anal. Chim. Acta*, 42 (1968) 127.
41 E. W. Baumann, *Anal. Chim. Acta*, 54 (1971) 189.
42 E. W. Baumann, *J. Electroanal. Chem.*, 34 (1972) 238.
43 E. W. Baumann, *J. Inorg. Nucl. Chem.*, 31 (1969) 3155.
44 E. W. Bazzelle, *Anal. Chim. Acta*, 54 (1971) 29.
45 *Beckman Select Ion Electrodes*, Bulletin 7145-A.
46 H. Bender and D. J. Pye, *U. S. Patent* 2 177 596, 17.5.1938.
47 J. Berger, A. I. Rachlin, W. E. Scott, C. H. Sternbach and M. W. Goldberg, *J. Amer. Chem. Soc.*, 73 (1951) 5295.
48 J. Bernstein, *Pfluegers Arch. Gesamte Physiol.*, 92 (1902) 521.
49 D. S. Bernstein, M. A. Aliaponlions, R. S. Hattner, A. Wachman and B. Rose, *Endocrinol.*, 85 (1969) 589.
50 A. Bethe and T. Toropoff, *Z. Phys. Chem.*, 88 (1914) 686.
51 R. Beutner, *Biochem. Z.*, 47 (1912) 73.
52 R. Beutner, *Z. Elektrochem.*, 19 (1931) 319.
53 W. J. Blaedel, D. B. Easty, L. Anderson and T. R. Farrell, *Anal. Chem.*, 43 (1971) 890.
54 J. A. Blay and J. H. Ryland, *Anal. Lett.*, 4 (1971) 653.
55 R. Bloch, A. Shatkay and H. A. Saroff, *Biophys. J.*, 7 (1967) 865.
56 R. Bock and H.-J. Puff, *Z. Anal. Chem.*, 240 (1968) 381.
57 R. Bock and S. Strecker, *Z. Anal. Chem.*, 235 (1968) 322.
58 A. M. Bond and G. Heftner, *Inorg. Chem.*, 9 (1970) 1021.
59 A. M. Bond and T. A. O'Donell, *J. Electroanal. Chem.*, 26 (1970) 137.
60 O. D. Bonner and D. C. Lunney, *J. Phys. Chem.*, 70 (1966) 1140.
61 S. K. Bose, *J. Indian Chem. Soc.*, 37 (1960) 465.
62 L. Boulares-Poinsignon, J. Adamy and P. Federlin, *C. R.*, 268 (1969) 1894.
63 L. I. Braddock, I. Nagelberg, E. Margallo and G. J. Barbero, *Cystic Fibrosis Club Abstr.*,April 29 (1969) 17.
64 M. J. Brand and G. A. Rechnitz, *Anal. Chem.*, 42 (1970) 478.
65 M. J. D. Brand and G. A. Rechnitz, *Anal. Chem.*, 42 (1970) 1172.
66 M. J. D. Brand and G. A. Rechnltz, *Anal. Chem.*, 42 (1970) 1659.
67 J. M. Bremner, L. G. Bundy and A. S. Agarwal, *Anal. Lett.*, 1 (1968) 837.
68 M. I. Brittan, N. W. Hanf and R. R. Liebenberg, *Anal. Chem.*, 42 (1970) 1306.
69 H. Brockmann and G. Schmidt-Kastner, *Chem. Ber.*, 88 (1955) 57.
70 H. R. Bronstein and D. L. Manning, *J. Electrochem. Soc.*, 119 (1972) 125.
71 L. G. Bruton, *Anal. Chem.*, 43 (1971) 579.
72 E. B. Buchanan and J. L. Seago, *Anal. Chem.*, 40 (1968) 517.
73 M. Buck and G. Reusman, *Fluoride*, 4 (1971) 5.
74 R. P. Buck, *Anal. Chem.*, 40 (1968) 1432.

75 R. P. Buck, in A. Weissberger and B. W. Rossiter, *Physical Methods of Chemistry*, Part IIA, Interscience, New York, 1971, Chap. II.
76 R. P. Buck, private communication.
77 N. G. Bunton and N. T. Crosby, *Water Treat. Exam.*, 18 (1969) 338.
78 K. Burger and B. Pinter, *Hung. Sci. Instrum.*, 8 (1966) 11.
79 J. E. Burroughs and A. I. Attia, *Anal. Chem.*, 40 (1968) 2052.
80 M. A. Bush and M. R. Truter, *Chem. Commun.*, (1970) 1439.
81 J. N. Butler, *Biophys. J.*, 8 (1968) 1426.
82 J. N. Butler, *Thermodynamic Studies*, Chapter 5 of ref. 288.
83 J. N. Butler and R. Huston, *Anal. Chem.*, 42 (1970) 676.
84 J. N. Butler and R. Huston, *Anal. Chem.*, 42 (1970) 1308.
85 K. Cammann, *Beckman Report*, 1/70 (1970) 21.
86 R. M. Carlson and J. L. Paul, *Anal. Chem.*, 40 (1968) 1292.
87 R. M. Carlson and J. L. Paul, *Soil Sci.*, 108 (1969) 266.
88 R. A. Carter, *Proc. Ass. Clin. Biochem.*, 5 (1968) 67.
89 H. H. Cary and W. P. Baxter, *U.S. Patent* 2 462 843, 1945.
90 R. W. Cattral and H. Freiser, *Anal. Chem.*, 43 (1971) 1905.
91 A. A. Cernik, J. A. Cooke and R. J. Hall, *Nature*, 227 (1970) 1260.
92 P. M. Chalk and D. R. Keeney, *Nature*, 229 (1971) 42.
93 B. Chance and R. W. Estbrook, *Science*, 146 (1964) 957.
94 B. Chance and T. Yoshioka, *Biochem.*, 5 (1966) 3224.
95 *Chem. Eng. News*, 48, No. 9 (1970) 26.
96 *Chem. Eng. News*, 48, No. 27 (1970) 42.
96a S. Y. Chow, D. Kunze, A. M. Brown and D. M. Woodburg, *Proc. Nat. Acad. Sci.*, 67 (1970) 998.
97 G. Christian, *Anal. Lett.*, 3 (1970) 11.
98 J. J. Christensen, J. O. Hill and R. M. Izatt, *Science*, 174 (1971) 459.
99 S. Ciani, G. Eisenman and G. Szabó, *J. Membrane Biol.*, 1 (1969) 1.
100 C. J. Coetzee and A. J. Basson, *Anal. Chim. Acta*, 57 (1971) 478.
101 C. J. Coetzee and A. J. Basson, *Anal. Chim. Acta*, 56 (1971) 321.
102 C. J. Coetzee and H. Freiser, *Anal. Chem.*, 40 (1968) 2041.
103 C. J. Coetzee and H. Freiser, *Anal. Chem.*, 41 (1969) 1128.
104 Coleman, *The Completely New Coleman Ion-Activity Sensing System*, Bulletin B-329, 1968.
105 Coleman Instruments, *Bromide Ion-Selective Electrode* 3-801, October 1968.
106 Coleman Instruments, *Chloride Ion-Selective Electrode* 3-802, October 1968.
107 Coleman Instruments, *Copper Ion-Selective Electrode* 3-804, October 1968.
108 Coleman Instruments, *Fluoride Ion-Selective Electrode* 3-803, October 1968.
109 Coleman Instruments, *Sulfide Silver Ion-Selective Electrode* 3-805, October 1968.
110 H. B. Collier, *Anal. Chem.*, 42 (1970) 1443.
111 D. E. Collis and A. A. Diggens, *Water Treat. Exam.*, 18 (1969) 192.
112 F. J. Conrad, *Talanta*, 18 (1971) 952.
113 F. Conti and G. Eisenman, *Biophys. J.*, 5 (1965) 247.
114 F. Conti and G. Eisenman, *Biophys. J.*, 5 (1965) 511.
115 Corning–EEL Scientific Instruments, *pH and Ion-Selective Electrodes.*
115a M. C. Cornwall, D. F. Peterson, D. L. Kunze, J. L. Walker and A. M. Brown, *Brain Res.*, 23 (1970) 433.
116 R. A. Cosgrove, C. A. Mask and I. H. Krull, *Anal. Lett.*, 3 (1970) 457.
117 A. K. Covington, *Chem. Brit.*, 5 (1969) 388.
118 A. K. Covington, *Heterogeneous Membrane Electrodes*, Chapter 3 of ref. 288.
119 A. K. Covington, *Reference Electrodes*, Chapter 4 of ref. 288.
120 A. K. Covington and J. M. Thain, *Anal. Chim. Acta*, 55 (1971) 453.
121 M. Cremer, *Z. Biol.*, 47 (1906) 562.
122 E. F. Croomes and R. C. McNutt, *Analyst*, 93 (1968) 729.
123 N. T. Crosby, *J. Appl. Chem.*, 19 (1969) 100.
124 N. T. Crosby, A. L. Dennis and J. G. Stevens, *Analyst*, 93 (1968) 643.
125 G. L. Crossman and W. Selig, *Informal report UCID*-15444, Lawrence Radiation Laboratory, University of California, Livermore, Calif., February 1969.
126 B. Csakvari and K. Meszaros, *Hung. Sci. Instrum.*, 11 (1968) 9.
127 R. W. Cummins, *Detergent Age*, March 1968, p. 22.

128 D. J. Curran and K. S. Fletcher, *Anal. Chem.*, 41 (1969) 267.
129 H. Dahms, R. Rock and D. Seligson, *Clin. Chem.*, 14 (1969) 859.
130 J . F. Danielli and H. Davson, *J. Cell . Comp. Physiol.*, 5 (1935) 495.
131 J. DeMoura, D. LeTourneau and A. C. Wiese, *Arch. Biochem. Biophys.*, (1969) 258.
132 H. Diebler, M. Eigen, G. Ilgenfritz, G. Maass and R. Winkler, *Pure Appl. Chem.*, 20 (1969) 93.
133 B. Dietrich, J. M. Lehn and J. P. Sauvage, *Chem. Commun.*, (1970) 1056.
134 B. Dietrich, J. M. Lehn and J. P. Sauvage, *Tetrahedron Lett.*, 34 (1970) 2885, 2889.
135 J. S. DiGregorio and M. D. Morris, *Anal. Chem.*, 42 (1970) 94.
136 J. S. DiGregorio and M. D. Morris, *Anal. Lett.*, 1 (1968) 811.
137 R. DiMartini, *Anal. Chem.*, 42 (1970) 1102.
138 T. N. Dobbelstein and H. Diehl, *Talanta*, 16 (1969) 1341.
139 M. Dole, *J. Chem. Phys.*, 2 (1934) 862.
140 M. Dole, *The Glass Electrode*, New York, 1941.
141 J. Dominguez, J. D. Danitz, H. Gerloch and V. Prelog, *Helv. Chim. Acta*, 45 (1962) 129.
142 F. G. Donnan, *Z. Elektrochem.*, 17 (1911) 572.
143 R. H. Doremus, *Diffusion Potentials in Glass*, Chapter 4 of ref. 205.
144 E. Du Bois-Reymond, *Untersuchungen über thierische Elektricität*, Vol. I, Berlin, 1848; Vol. II/1, Berlin, 1849; Vol. II/2, Berlin, 1884.
145 E. J. Duff and J. L. Stuart, *Anal. Chim. Acta*, 57 (1971) 233.
145a R. A. Durst, *Amer. Sci.*, 59 (1971) 354.
146 R. A. Durst, *Anal. Chem.*, 40 (1968) 931.
147 R. A. Durst, *Analytical Techniques and Application of Ion-Selective Electrodes*, Chapter 11 of ref. 288.
148 R. A. Durst, *Mikrochim. Acta*, 3 (1969) 611.
149 R. A. Durst and B. T. Duhart, *Anal. Chem.*, 42 (1970) 1002.
150 R. A. Durst and J. W. Ross, *Anal. Chem.*, 40 (1968) 1343.
151 R . A. Durst and J. K. Taylor, *Anal. Chem.*, 39 (1967) 1483.
152 J. L. Dye, M. G. DeBaker and V. A. Nicely, *J. Amer. Chem. Soc.*, 92 (1970) 5226.
153 C. R. Edmond, *Anal. Chem.*, 41 (1969) 1327.
154 C. R. Edmond, *Bull. Aust. Min. Dev. Lab.*, (1969) 1.
155 G. Eisenman, *Anal. Chem.*, 40 (1968) 310.
156 G. Eisenman, *Biophys. J.*, 2, Part 2, Suppl., 259 (1962).
157 G. Eisenman, *Particular Properties of Cation-Selective Glass Electrodes Containing* Al_2O_3, Chapter 9 of ref. 66.
158 G. Eisenman, in C. W. Reilley, *Advances in Analytical Chemistry and Instrumentation*, Vol. 4, J. Wiley, New York, 1965, p. 213.
159 G. Eisenman, *The Origin of the Glass-Electrode Potential*, Chapter 5 of ref. 205.
160 G. Eisenman, *Theory of Membrane Electrode Potential: an Examination of the Parameters Determining the Selectivity of Solid and Liquid Ion Exchangers and of Neutral Sequestering Molecules*, Chapter 1 of ref. 288.
161 G. Eisenman, *Physical Basis of the Ionic Specificity of the Glass Electrode*, Chapter 7 of ref. 205.
162 G. Eisenman, in A. Kleinzeller and A. Kotyk, *Symposium on Membrane Transport and Metabolism*, Academic Press, New York, 1961, p. 163.
163 G. Eisenman, S. Ciani and G. Szabo, *J. Membrane Biol.*, 1 (1969) 294.
164 G. Eisenman , S. Ciani and G. Szabo, *Fed. Proc.*, 27 (1968) 1289.
165 G. Eisenman , D. O. Rudin and J. U. Casby, *Science*, 126 (1957) 831.
166 Electronic Instruments Ltd., *Information sheet TDS-ELECT*-13, Issue 1, March 1965.
167 L. A. Elfers and C. E. Decker, *Anal. Chem.*, 40 (1968) 1658.
168 B. F. Erlanger and R. A. Sack, *Anal. Biochem.*, 33 (1970) 318.
169 S. Estrada-O., S. N. Graven and H. A. Lardy, *J. Biol. Chem.*, 242 (1967) 2925.
170 L. Evans, R. D. Hoyle and J. B. Macaskill, *N. Z. J. Sci.*, 13 (1970) 143.
171 E. Eyal and G. A. Rechnitz, *Anal. Chem.*, 43 (1971) 1090.
172 A. B. Falcone and H. O. Hadler, *Arch. Biochem. Biophys.*, 124 (1968) 91, 115.
173 W. P. Ferren and N. A. Shane, *J. Food Sci.*, 34 (1969) 317.
174 W. Fertl and F. W. Jessen, *Clays Clay Miner.*, (1969) 17.
175 R. B. Fischer and R. F. Babcock, *Anal. Chem.*, 30 (1958) 1732.
176 B. Fleet and H. v. Storp, *Anal. Chem.*, 43 (1971) 1575.
177 B. Fleet and G. A. Rechnitz, *Anal. Chem.*, 42 (1970) 690.

178 K. S. Fletcher III and R. F. Mannion, *Anal. Chem.*, 42 (1970) 285.
179 T. M. Florence, *J. Electroanal. Chem.*, 31 (1971) 77.
180 Foxboro, *Chloride Ion Measuring Electrode, GS* 1-3*F* 1*C*, April 1970.
181 Foxboro, *Cyanide Ion Measuring Electrode, GS* 1-3*F* 1 *G*, April 1970.
182 Foxboro, *Fluoride Ion Measuring Electrode, GS* 1-3*F* 1 *H*, April 1970.
183 Foxboro, *Model* 32 *FMS—A Fluoride Measuring System, GS* 6-1*A*2*A*, June 1968.
184 Foxboro, *Sulfide Ion Measuring Electrode, GS* 1-3*F* 1 *D*, April 1970.
185 H. J. Francis, J. H. Deomarine and D. D. Persing, *Microchem. J.*, 14 (1969) 580.
186 M. Frant, *U.S. Patent* 3 431 182, 1968.
187 M. S. Frant, *Plating*, 54 (1967) 702.
188 M. S. Frant and J. W. Ross, *Anal. Chem.*, 40 (1968) 1169.
189 M. S. Frant and J. W. Ross, *Science*, 154 (1966) 1553.
190 M. S. Frant and J. W. Ross, *Science*, 167 (1970) 987.
191 M. S. Frant and J. W. Ross, *TAPPI*, 53 (1970) 1753.
192 H. K. Frensdorff, *J. Amer. Chem. Soc.*, 93 (1971) 600.
193 S. M. Friedman, *H^+ and Cation Analysis in Biological Fluids in the Intact Animal*, Chapter 16 of ref. 205.
194 P. N. Früh, J. T. Clerc and W. Simon, *Helv. Chim. Acta*, 54 (1971) 1445.
195 B. W. Fry and D. R. Taves, *J. Lab. Clin. Med.*, 75 (1970) 1020.
196 P. Gachon, A. Kergomard and H. Veschambre, *Chem. Commun.*, (1970) 1421.
197 H. Gamsjäger, P. Schindler and B. Kleinert, *Chimia*, 23 (1969) 229.
198 G. Gardner and G. H. Nancollas, *Anal. Chem.*, 42 (1970) 794.
199 J. E. Garvin, *J. Cell. Physiol.*, 72 (1969) 197.
200 G. F. Gause and M. G. Brazhnikova, *Lancet*, 247 (1944) 715.
201 C. Gavach, *C. R.*, 273 (1971) 489.
202 D. G. Gehring, W. A. Dippel and R. S. Boucher, *Anal. Chem.*, 42 (1970) 1686.
203 J. W. Gibbs, *Collected Works*, Vol. 1, Longmans, Green, New York, 1928, p. 83.
204 J. T. Gillingham, M. M. Shirer and N. R. Page, *Agron. J.*, 61 (1969) 717.
205 G. Eisenman (Editor), *Glass Electrodes for Hydrogen and Other Cations, Principles and Practice*, Marcel Dekker, New York, 1967.
206 D. E. Goldman, *J. Gen. Physiol.*, 27 (1943) 37.
207 M. Goldman and L. Shen, *Phys. Rev.*, 144 (1966) 321.
208 Goodman, *IADR Abstr.*, (1969) 150.
209 V. A. Gotlib, E. P. Buzhinsky and A. A. Lev, *Biofiz.*, 13 (1968) 562.
210 G. Gran, *Acta Chem. Scand.*, 4 (1950) 559.
211 G. Gran, *Analyst*, 77 (1952) 661.
212 S. N. Graven, H. A. Lardy and S. Estrado-O., *Biochem.*, 6 (1967) 365.
213 S. N. Graven, H. A. Lardy, D. Johnson and A. Rutter, *Biochem.*, 5 (1966) 1729.
214 S. N. Graven, H. A. Lardy and A. Rutter, *Biochem.*, 5 (1966) 1735.
215 H. P. Gregor and H. Schonborn, *J. Amer. Chem. Soc.*, 79 (1957) 1507.
216 H. P. Gregor and H. Schonborn, *J. Amer. Chem. Soc.*, 81 (1959) 3911.
217 H. P. Gregor and H. Schonborn, *J. Amer. Chem. Soc.*, 83 (1961) 3576.
218 H. P. Gregor and K. Sollner, *J. Phys. Chem.*, 58 (1954) 409.
219 P. Grøn, H. G. McCann and F. Brudevold, *Arch. Oral Biol.*, 13 (1968) 203.
220 P. Grøn, M. A. Spinelli and D. I. Hay, *IADR Abstr.*, (1968) 58.
221 P. Grøn, K. Yao and M. Spinelli, *J. Dent. Res.*, Suppl. to No. 5, 48 (1969) 709.
222 L. C. Gruen and B. S. Harrap, *Anal. Biochem.*, 42 (1971) 377.
223 E. A. Guggenheim, *J. Amer. Chem. Soc.*, 52 (1930) 1315.
224 E. A. Guggenheim, *Thermodynamics*, North Holland, Amsterdam, 1949.
225 G. G. Guilbault and P. J. Brignac, *Anal. Chem.*, 41 (1969) 1136.
226 G. G. Guilbault and P. J. Brignac, *Anal. Chim. Acta*, 56 (1971) 139.
227 G. G. Guilbault and E. Hrabánková, *Anal. Chem.*, 42 (1970) 1779.
228 G. G. Guilbault and E. Hrabánková, *Anal. Chim. Acta*, 52 (1970) 287.
229 G. G. Guilbault and E. Hrabánková, *Anal. Lett.*, 3 (1970) 53.
230 G. G. Guilbault and J. Montalvo, *Anal. Lett.*, 2 (1969) 283.
231 G. G. Guilbault and J. Montalvo, *J. Amer. Chem. Soc.*, 91 (1969) 2164.
232 G. G. Guilbault and J. Montalvo, *J. Amer. Chem. Soc.*, 92 (1970) 2533.

233 G. G. Guilbault, R. K. Smith and J. Montalvo, *Anal. Chem.*, 41 (1969) 600.
234 G. G. Guilbault and F. R. Shu, *Anal. Chim. Acta*, 56 (1971) 333.
235 J.-L. Guth and R. Wey, *Bull. Soc. Fr. Miner. Cristallogr.*, 92 (1969) 105.
236 B. György, L. André, E. Stehli and E. Pungor, *Anal. Chim. Acta*, 40 (1969) 318.
237 F. Haber, *Ann. Phys.*, (4) 26 (1908) 927.
238 F. Haber and Z. Klemensiewicz, *Z. Phys. Chem.*, 67 (1909) 385.
239 T. P. Hadjiioannou and D. S. Papastathopoulos, *Talanta*, 17 (1970) 399.
240 H. I. Hadler and A. B. Falcone, *Arch. Biochem. Biophys.*, 124 (1968) 110.
241 E. Hakoila, *Anal. Lett.*, 3 (1970) 273.
242 D. K. Hale and D. J. McCauley, *Trans. Faraday Soc.*, 57 (1961) 135.
243 F. M. Hall and S. J. Slater, *Aust. J. Chem.*, 21 (1968) 1663.
244 R. L. Hamill, C. E. Higgens, H. E. Boaz and M. Gorman, *Tetrahedron Lett.*, 49 (1969) 4255.
244a M. E. Haney and M. M. Hoehn, *Antimicrobial Agents Chemotherapy*, 1967, p. 349.
245 L. Hansen, M. Buechele, J. Koroschec and W. J. Warwick, *Amer. J. Clin. Pathol.*, 49 (1968) 834.
245a R. L. Harned, P. H. Hidy, C. J. Corum and K. L. Jones, *Proc. Indiana Acad. Sci.*, 59 (1950) 38.
246 B. S. Harrap and L. C. Gruen, *Anal. Biochem.*, 42 (1971) 398.
247 E. J. Harris, R. Cockrell and B. C. Pressman, *Biochem. J.*, 99 (1966) 200.
248 R. C. Harris and H. H. Williams, *Appl. Meteorol.*, 8 (1969) 299.
249 J. E. Harwood, *Water Res.*, 3 (1969) 273.
250 C. Harzdorf, *Z. Anal. Chem.*, 245 (1969) 67.
251 R. S. Hattner, J. W. Johnson, D. S. Bernstein, A. Wachman and J. Brackman, *Clin. Chim. Acta*, 28 (1970) 67.
252 J. Havas, *Proc. 2nd Conf. Appl. Phys. Chem., Veszprém, Hungary*, 1971, p. 631.
253 J. Havas, M. Huber, I. Szabo and E. Pungor, *Hung. Sci. Instrum.*, 9 (1967) 1923.
254 J. Havas, E. Papp and E. Pungor, *Acta Chim. Acad. Sci. Hung.*, 58 (1968) 9.
255 J. Havas and E. Pungor, *Proc. IMEKO Symposium on Electrochemical Sensors, Veszprém*, 1968, p. 79.
256 D. A. Haydon, *J. Amer. Oil Chem. Soc.*, 45 (1968) 230.
257 D. A. Haydon, The Organization and Permeability of Artificial Lipid Membranes, Chapter 3, in E. E. Bittar, *Membranes and Ion Transport*, Wiley, New York, 1970, p. 64.
258 D. H. Haynes, A. Kowalsky and B. C. Pressman, *J. Biol. Chem.*, 244 (1969) 502.
259 W. M. Haynes and J. H. Wagenknecht, *Anal. Lett.*, 4 (1971) 491.
260 M. H. Hebb, *J. Chem. Phys.*, 20 (1952) 185.
261 F. Helfferich, *Ionenaustauscher* I, Verlag Chemie, Weinheim, 1959, p. 54, 305.
262 P. Henderson, *Z. Phys. Chem.*, 59 (1907) 118.
263 P. Henderson, *Z. Phys. Chem.*, 63 (1908) 325.
264 T. Higuchi, C. R. Illian and J. L. Tossounian, *Anal. Chem.*, 42 (1970) 1674.
265 J. A. M. Hinke, *Cation-Selective Microelectrodes for Intracellular Use*, Chapter 17 of ref. 205.
266 H. Hirata and K. Date, *Anal. Chem.*, 43 (1971) 279.
267 H. Hirata and K. Date, *Talanta*, 17 (1970) 883.
268 H. Hirata and K. Higashiyama, *Bull. Chem. Soc. Jap.*, 44 (1971) 2420.
269 H. Hirata and K. Higashiyama, *Anal. Chim. Acta*, 54 (1971) 415.
270 H. Hirata and K. Higashiyama, *Anal. Chim. Acta*, 57 (1971) 476.
271 H. Hirata, K. Higashiyama and K. Date, *Anal. Chim. Acta*, 51 (1970) 209.
272 R. F. Hirsch and J. D. Portock, *Anal. Lett.*, 2 (1969) 295.
273 D. I. Hitchcock, in T. Shedlovsky, *Electrochemistry in Biology and Medicine*, Interscience, New York, 1955, p. 6.
273a P. Hnik, F. Vyskočil, N. Kříž and M. Holas, *Brain Res.*, 40 (1972) 559.
274 A. L. Hodgkin, *Proc. R. Soc. (London)*,B 148 (1958) 1.
275 A. L. Hodgkin and A. F. Huxley, *J. Physiol. (London)*, 117 (1952) 500.
276 A. L. Hodgkin and B. Katz, *J. Physiol. (London)*, 108 (1949) 37.
277 V. H. Holsinger, L. P. Posati and M. J. Pallansch, *J. Dairy Sci.*, 50 (1967) 1189.
278 W. L. Hoover, J. R. Melton and P. A. Howard, *J. Ass. Offic. Anal. Chem.*, 54 (1971) 760.
279 K. Horowitz, *Z. Phys. Chem.*, 115 (1925) 424.
280 P. Hotz, H. R. Mühlemann and A. Schait, *Helv. Odontol. Acta*, 14 (1970) 26.
281 K. Hozumi and N. Akimoto, *Jap. Anal.*, 20 (1971) 467.
282 T. M. Hseu and G. A. Rechnitz, *Anal. Chem.*, 40 (1968) 1054, 1661.
283 T. M. Hseu and G. A. Rechnitz, *Anal. Lett.*, 1 (1968) 629.

284 W. S. Hughes, *J. Chem. Soc.*, (1928) 491.
285 R. Huston and J. N. Butler, *Anal. Chem.*, 41 (1969) 200.
286 N. Ibl, Application of Mass Transfer Theory, The Formation of Powdered Metal Deposits, in P. Delahay and C. W. Tobias, *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 2, J. Wiley, New York, 1962, p. 88.
287 B. L. Ingram, *Anal. Chem.*, 42 (1970) 1825.
288 R. A. Durst (Editor), *Ion-Selective Electrodes*, Natl. Bur. Stand. Spec. Publ. 314, Washington, 1969.
289 J. O. Isard, *Nature*, 184 (1959) 1616.
290 J. O. Isard, *The Dependence of Glass-Electrode Properties on Composition*, Chapter 3 of ref. 205.
291 N. Ishibashi and H. Kahara, *Anal. Lett.*, 4 (1971) 785.
292 *Israel Patent No.* 21709, 1966.
293 V. T. Ivanov, I. A. Laine, N. D. Abdulayev, L. B. Senyavina, E. M. Popov, Yu. A. Ovchinnikov and M. M. Shemyakin, *Biochem. Biophys. Res. Commun.*, 34 (1969) 803.
294 V. T. Ivanov, A. I. Miroshnikov, N. D. Abdullaev, L. B. Senyavina, S. F. Arkhipova, N. N. Uvarova, K. Kh. Khalilulina, V. F. Bystrov and Yu. A. Ovchinnikov, *Biochem. Biophys. Res. Commun.*, 42 (1971) 654.
295 D. J. G. Ives and G. J. Janz, *Reference Electrodes*, Academic Press, New York, 1961.
296 R. M. Izatt, D. P. Nelson, J. H. Rytting, B. L. Haymore and J. J. Christensen, *J. Amer. Chem. Soc.*, 93 (1971) 1619.
297 R. M. Izatt, J. H. Rytting, D. P. Nelson, B. I. Haymore and J. J. Christensen, *Science*, 164 (1969) 443.
298 W. Jaenicke, *Z. Elektrochem.*, 55 (1951) 648.
299 W. Jaenicke and M. Haase, *Z. Elektrochem.*, 63 (1959) 521.
300 D. Jagner, *Acta Univ. Gothob.*, Dissertation Abstr., Gothenburg, 1971.
301 D. Jagner and K. Årén, *Anal. Chim. Acta*, 57 (1971) 185.
302 B. Jaselskis and M. K. Bandemer, *Anal. Chem.*, 41 (1969) 855.
303 J. D. Johnson and E. D. Daugherty, *Univ. of N. C. School of Public Health, Dept. of Environ. Sci. and Eng., Publ. No.* 117, 1969.
304 J. R. Johnson, R. H. Bristow and H. H. Blau, *J. Amer. Ceram. Soc.*, 34 (1951) 165.
304a B. C. Jones, J. E. Heveran and B. Z. Senkowski, *J. Pharm. Sci.*, 58 (1969) 607.
305 D. E. Jordan, *J. Ass. Offic. Agr. Chem.*, 53 (1970) 447.
306 K. M. Joshi and N. P. Suryanarayana, *J. Indian Chem. Soc.*, 45 (1968) 537.
307 G. J. Kakabadse, B. Manohin, J. M. Bather, E. C. Weller and P. Woodbridge, *Nature*, 229 (1971) 626.
308 R. K. Kaminski, *Instrum. Technol.*, 16 (1969) 41.
309 G. Karreman and G. Eisenman, *Bull. Math. Biophys.*, 24 (1962) 413.
310 N. A. Kazarjan and E. Pungor, *Anal. Chim. Acta*, 51 (1970) 213.
311 B. Katz, *Nerve, Muscle and Synapse*, McGraw Hill, New York, 1966.
312 P. J. Ke, L. W. Regier and H. E. Power, *Anal. Chem.*, 41 (1969) 1081.
313 D. R. Keeney, B. H. Byrnes and J. J. Genson, *Analyst*, 95 (1970) 383.
314 J. R. Kerns, *Technical Report AFML-TR*-68-273, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, February 1969.
315 D. R. Kester and R. M. Pytkowicz, *Limnol. Oceanogr.*, 13 (1968) 670.
316 D. R. Kester and R. M. Pytkowicz, *Limnol. Oceanogr.*, 14 (1969) 686.
317 R. N. Khuri, *Glass Microelectrodes and their Uses in Biological Systems*, Chapter 18 of ref. 205.
318 R. N. Khuri, *Ion-Selective Electrodes in Biomedical Research*, Chapter 8 of ref. 288.
319 B. T. Kilbourn, J. D. Danitz, L. A. R. Pioda and W. Simon, *J. Mol. Biol.*, 30 (1967) 559.
320 J. A. King and A. K. Mukherji, *Naturwiss.*, 53 (1966) 702.
321 D. Klockow, H. Ludwig and M. A. Girando, *Anal. Chem.*, 42 (1970) 1682.
322 J. Knoeck, *Anal. Chem.*, 41 (1969) 2069.
323 E. Koch and C. Wagner, *Z. Phys. Chem.*, (B)38 (1937) 295.
324 I. M. Kolthoff and H. L. Sanders, *J. Amer. Chem. Soc.*, 59 (1937) 416.
325 L. Kopito and H. Schwachman, *Pediatr.*, 43 (1969) 794.
326 S. Kopolow, T. E. H. Esch and J. Smid, *Macromol.*, 4 (1971) 359.
326a J. Koryta, *Iontově selektivní membránové elektrody* (*Ion-Selective Membrane Electrodes*), Academia, Prague, 1972.
327 J. Koryta, J. Dvořák and V. Boháčková, *Electrochemistry*, Methuen, London, 1970.
327a J. Koryta and M. L. Mittal, *J. Electroanal. Chem.*, 36 (1972) App. 14.
328 R. Krämer and H. Lagoni, *Naturwiss.*, 56 (1969) 36.

329 S. Krasne, H. Eisenman and G. Szabo, *Science*, 174 (1971) 412.
330 L. Kratz, *Die Glaselektrode und ihre Anwendungen*, Frankfurt a.M., 1950.
331 W. Krijgsman, J. F. Mansveld and B. Griepink, *Clin. Chim. Acta*, 29 (1970) 575.
331a N. Kříž, F. Vyskočil and P. Hník, *Physiologia Bohemoslovenica*, 21 (1972).
332 P. A. Kryukov and A. A. Kryukov, *U.S.S.R. Patent* 51509, 31.7.1937.
333 I. H. Krull, C. A. Mask and R. E. Cosgrove, *Anal. Lett.*, 3 (1970) 43.
334 T. Kubata, S. Matsitani, M. Shiro and H. Koyama, *Chem. Commun.*, (1968) 1541.
335 R. L. LaCroix, D. R. Keeney and L. M. Walsh, *Soil Sci. Plant Anal.*, 1 (1970) 1.
336 S. Lal and G. D. Christian, *Anal. Lett.*, 3 (1970) 11.
337 N. Lakshminarayanaish, *Chem. Rev.*, 65 (1965) 691.
338 S. Lal and G. D. Christian, *Anal. Chem.*, 43 (1971) 410.
339 D. Langmuir and R. L. Jacobson, *Environ. Sci. Technol.*, 4 (1970) 834.
340 H. A. Lardy, S. N. Graven and S. Estrada-O., *Fed. Proc.*, 26 (1967) 1355.
341 H. A. Lardy, D. Johnson and W. C. McMurray, *Arch. Biochem. Biophys.*, 78 (1958) 587.
342 T. G. Lee, *Anal. Chem.*, 41 (1969) 391.
343 J. M. Lehn and J. P. Sauvage, *Chem. Commun.*, (1971) 440.
344 B. Lengyel and E. Blum, *Trans. Faraday Soc.*, 30 (1934) 461.
345 A. Lerman and A. Shatkay, *Earth Planet. Sci. Lett.*, 5 (1968) 63.
346 A. A. Lev and E. P. Buzhinský, *Tsitol.*, 9 (1967) 106.
347 D. A. Levaggi, W. Oyung and M. Feldstein, *J. Air Pollut. Assoc.*, 21 (1971) 277.
348 R. J. Levins, *Anal. Chem.*, 43 (1971) 1045.
349 G. N. Lewis and L. W. Sargent, *J. Amer. Chem. Soc.*, 31 (1909) 363.
350 J. V. Leyendekkers, *Anal. Chem.*, 43 (1971) 1835.
351 J. V. Leyendekkers and M. Whitfield, *Anal. Chem.*, 43 (1971) 322.
352 J. V. Leyendekkers and M. Whitfield, *J. Phys. Chem.*, 75 (1971) 957.
353 T. K. Li and J. T. Piechocki, *Clin. Chem.*, 17 (1971) 411.
354 A. Liberti and M. Mascini, *Anal. Chem.*, 41 (1969) 676.
355 T. S. Light, *Industrial Analysis and Control with Ion Selective Electrodes*, Chapter 10 of ref. 288.
356 T. S. Light, *Industrial Water Engineering*, September, 1969.
357 T. S. Light and R. F. Mannion, *Anal. Chem.*, 41 (1969) 107.
358 T. S. Light and J. L. Swartz, *Anal. Lett.*, 1 (1968) 825.
359 J. J. Lingane, *Anal. Chem.*, 39 (1967) 881.
360 J. J. Lingane, *Anal. Chem.*, 40 (1968) 935.
361 R. A. Llenado and G. A. Rechnitz, *Anal. Chem.*, 43 (1971) 1457.
362 R. Luther, *Z. Phys. Chem.*, 19 (1896) 529.
363 W. K. Lutz, P. U. Früh and W. Simon, *Helv. Chim. Acta*, 54 (1971) 2767.
364 W. K. Lutz, H.-K. Wipf and W. Simon, *Helv. Chim. Acta*, 53 (1970) 1741.
365 J. C. MacDonald and G. P. Slater, *Can. J. Biochem.*, 46 (1968) 573.
366 A. M. G. Macdonald and K. Tóth, *Anal. Chim. Acta*, 27 (1968) 63.
367 D. A. MacInnes, *The Principles of Electrochemistry*, New York, 1939, p. 220–245, 461–465.
368 D. A. MacInnes and M. Dole, *J. Amer. Chem. Soc.*, 52 (1930) 29.
369 D. A. MacInnes and Y. L. Yeh, *J. Amer. Chem. Soc.*, 43 (1921) 2563.
370 A. R. Mack and R. B. Sanderson, *Can. J. Soil Sci.*, 51 (1971) 95.
371 M. K. Mahendrappa, *Soil Sci.*, (1969) 132.
372 H. Malissa and G. Jellinek, *Z. Anal. Chem.*, 245 (1969) 70.
373 H. Malmvig, *Introduction to Radiometer Selectrodes, ST* 56, Radiometer A/S.
374 S. E. Manahan, *Anal. Chem.*, 42 (1970) 128.
375 S. E. Manahan, *Appl. Microbiol.*, 18 (1969) 479.
376 Manual of Symbols and Terminology for Physicochemical Quantities and Units, *Pure Appl. Chem.*, 21 (1970) 1.
377 R. L. Markus, *Chimia*, 24 (1970) 372.
378 A. Marton and E. Pungor, *Anal. Chim. Acta*, 54 (1971) 209.
379 M. Mascini, *Anal. Chim. Acta*, 56 (1971) 316.
380 M. Mascini and A. Liberti, *Anal. Chim. Acta*, 47 (1969) 339.
381 M. Mascini and A. Liberti, *Anal. Chim. Acta*, 51 (1970) 231.
382 M. Matsui and H. Freiser, *Anal. Lett.*, 3 (1970) 191.
383 G. Mattock and D. M. Band, *Interpretation of pH and Cation Measurement*, Chapter 2 of ref. 205.

384 D. F. Mayers and D. W. Urry, *J. Amer. Chem. Soc.*, 94 (1972) 77.
385 H. G. McCann, *Arch. Oral Biol.*, 13 (1968) 475.
386 E. F. McFarren, B. J. Moorman and J. H. Parker, *Environ. Contam. Adm., Public Health Service Publ. No.* 1895, 1969.
387 S. G. A. McLaughlin, G. Szabo, G. Eisenman and S. Ciani, *Biophys. Soc. Abstr.*, 10 (1970) 96a.
388 E. O. McLean, G. H. Snyder and R. E. Franklin, *Soil Sci. Soc. Amer. Proc.*, 33 (1969) 388.
389 W. C. McMurray and R. W. Begg, *Arch. Biochem. Biophys.*, 84 (1959) 546.
390 R. E. Mesmer, *Anal. Chem.*, 40 (1968) 443.
391 R. E. Mesmer and C. F. Baes, *Inorg. Chem.*, 8 (1969) 618.
392 K. H. Meyer and J. F. Sievers, *Helv. Chim. Acta*, 19 (1936) 649, 665.
393 K. H. Meyer and J. F. Sievers, *Trans. Faraday Soc.*, 33 (1937) 1073.
394 L. Michaelis, *Kolloid-Z.*, 62 (1933) 2.
395 L. Michaelis and A. Fujita, *Biochem. Z.*, 158 (1925) 28.
396 L. Michaelis and K. Hayashi, *Biochem. Z.*, 173 (1926) 411.
397 P. J. Milham, *Analyst*, 95 (1970) 758.
398 A. Mirna, *Z. Anal. Chem.*, 254 (1971) 114.
399 P. Mitchell, in E. E. Bittar, *Membranes and Ion Transport*, Wiley, New York, 1970, Chap. 7.
400 H. H. Moeken, H. Eschrich and G. Willeborts, *Anal. Chim. Acta*, 45 (1969) 233.
401 M. S. Mohan and G. A. Rechnitz, *J. Amer. Chem. Soc.*, 92 (1970) 5839.
402 G. J. Moody, R. B. Oke and J. D. R. Thomas, *Analyst*, 95 (1970) 910.
402a G. J. Moody and J. D. R. Thomas, *Talanta*, 18 (1971) 1251.
403 C. Moore and B. C. Pressman, *Biochem. Biophys. Res. Commun.*, 15 (1964) 562.
404 E. W. Moore, *Ann. N. Y. Acad. Sci.*, (1968) 93.
405 E. W. Moore, *Hydrogen and Cation Analysis in Biological Fluids In Vitro*, Chapter 15 of ref. 205.
406 E. W. Moore, *J. Clin. Invest.*, 49 (1970) 318.
407 E. W. Moore, *Studies with Ion-Exchange Calcium Electrodes in Biological Fluids, Some Applications in Biomedical Research and Clinical Medicine*, Chapter 7 of ref. 288.
408 E. W. Moore and A. L. Blum, *J. Clin. Invest.*, 47 (1968) 70a.
409 E. W. Moore and G. M. Makhlouf, *Gastroenterol.*, 55 (1968) 465.
410 E. W. Morf and W. Simon, *Helv. Chim. Acta*, 54 (1971) 2683.
411 E. A. Moya and K. L. Cheng, *Anal. Chem.*, 42 (1970) 1669.
412 P. Mueller and D. O. Rudin, *Biophys. Biochem. Res. Commun.*, 26 (1967) 398.
413 P. Mueller and D. O. Rudin, *Theor. Biol.*, 18 (1968) 222.
414 P. Mueller, D. O. Rudin, H. T. Tien and W. C. Westcott, *Circ.*, 26 (1963) 1167.
415 P. Mueller, D. O. Rudin, H. T. Tien and W. C. Westcott, *Nature*, 194 (1962) 979.
416 A. K. Mukherji, *Anal. Chim. Acta*, 40 (1968) 354.
417 P. J. Muldoon and B. J. Liska, *J. Dairy Sci.*, 52 (1969) 460.
418 P. J. Muldoon and B. J. Liska, *J. Dairy Sci.*, 54 (1971) 117.
419 D. C. Müller, P. W. West and R. H. Müller, *Anal. Chem.*, 41 (1969) 2038.
420 G. Muto and K. Nozaki, *Jap. Anal.*, 18 (1969) 247.
421 R. J. K. Myers and E. A. Paul, *Can. J. Soil Sci.*, 48 (1968) 369.
422 P. Nagniot, *Beckman E.C. News*, 2 (1971) 10.
423 F. S. Nakayama, *Soil Sci.*, 106 (1968) 429.
424 F. S. Nakayama and B. A. Rasnick, *Anal. Chem.*, 39 (1967) 1022.
425 J. D. Neefus, J. Cholak and B. E. Saltzman, *Amer. Ind. Hyg. Ass. J.*, 31 (1970) 96.
426 W. Nernst, *Z. Phys. Chem.*, 2 (1888) 613.
427 W. Nernst, *Z. Phys. Chem.*, 4 (1889) 129.
428 W. Nernst and E. H. Riesenfeld, *Ann. Phys.*, (9) 8 (1902) 616.
429 G. Neumann, *Ark. Kem.*, 32 (1970) 229.
430 B. P. Nikolsky, *Zh. Fiz. Khim.*, 10 (1937) 495.
431 B. B. Nikolsky, *Zh. Fiz. Khim.*, 27 (1953) 724.
432 B. P. Nikolsky and M. M. Shults, *Vestn. Leningr. Univ.*, 4 (1963) 73.
433 B. B. Nikolsky and M. M. Shults, *Zh. Fiz. Khim.*, 36 (1962) 1327.
434 B. P. Nikolsky, M. M. Shults and A. A. Beliyustin, *Dokl. Akad. Nauk SSSR*, 144 (1962) 844.
435 B. P. Nikolsky, M. M. Shults, A. A. Beliyustin and A. A. Lev, *Recent Developments in the Ion-Exchange Theory of the Glass Electrode and its Applications in the Chemistry of Glass*, Chapter 6 of ref. 205.
436 B. P. Nikolsky and T. A. Tolmacheva, *Zh. Fiz. Khim.*, 10 (1937) 504.

437 B. Norén, *Acta Chem. Scand.*, 23 (1969) 931.
438 F. Oehme, *Chem. Rundsch.*, 21 (1968) 891.
439 F. Oehme, *Glas-Instr. Techn.*, 11 (1967) 1051.
440 F. Oehme, *Glas-Instr. Techn.*, 11 (1968) 1162.
441 M. Ohnishi and D. W. Urry, *Biochem. Biophys. Res. Commun.*, 34 (1969) 194.
442 A. Øien and A. R. Selmer-Olsen, *Analyst*, 94 (1969) 888.
443 R. T. Oliver and A. G. Clayton, *Anal. Chim. Acta*, 51 (1970) 409.
444 J. B. Orenberg and M. D. Morris, *Anal. Chem.*, 39 (1967) 1776.
445 I. Oreskes and K. S. Douglas, *Amer. Rheum. Ass. Annu. Meet.*, 1968, p. 502.
446 I. Oreskes, C. Hirsch, K. S. Douglas and S. Kupfer, *Clin. Chim. Acta*, 21 (1968) 303.
447 Orion Research, *Analytical Methods Guide*, October 1971.
448 Orion Research, *Instruction Manual, Potassium Ion Electrode, Model* 92-19, 1969.
449 *Orion Research Newsletter*, 1 (1969) No. 1.
450 *Orion Research Newsletter*, 1 (1969) No. 2.
451 *Orion Research Newsletter*, 1 (1969) No. 3.
452 *Orion Research Newsletter*, 1 (1969) No. 4.
453 *Orion Research Newsletter*, 1 (1969) No. 5.
454 *Orion Research Newsletter*, 1 (1969) No. 6.
455 *Orion Research Newsletter*, 1 (1969) No. 7.
456 *Orion Research Newsletter*, 2 (1970) No. 1.
457 *Orion Research Newsletter*, 2 (1970) No. 2.
458 *Orion Research Newsletter*, 2 (1970) No. 3 & 4.
459 *Orion Research Newsletter*, 2 (1970) No. 5 & 6.
460 *Orion Research Newsletter*, 2 (1970) No. 7 & 8.
461 *Orion Research Newsletter*, 2 (1970) No. 9 & 10.
462 *Orion Research Newsletter*, 2 (1970) No. 11 & 12.
463 *Orion Research Newsletter*, 3 (1971) No. 1 & 2.
464 *Orion Research Newsletter*, 3 (1971) No. 3 & 4.
465 *Orion Research Newsletter*, 3 (1971) No. 5 & 6.
466 *Orion Research Newsletter*, 3 (1971) No. 7 & 8.
467 W. Ostwald, *Z. Phys. Chem.*, 6 (1890) 71.
468 J. Ovchinnikov, *The Chemistry of Natural Depsipeptides, Recent Developments of Natural Carbon Compounds*, Vol. 2, Budapest, 1967, p. 3.
469 J. A. Ovchinnikov, *Vestn. Akad. Nauk SSSR*, 9 (1970) 49.
470 J. A. Ovchinnikov, V. T. Ivanov and I. I. Mikhaeva, *Tetrahedron Lett.*, (1971) 159.
471 J. A. Ovchinnikov, V. T. Ivanov and M. M. Shemyakin, in H. C. Beyerman, A. van de Linde and W. Maasen van den Brink, *Peptides*, North Holland Publ. Co., Amsterdam, 1967, p. 173.
472 J. L. Owades, S. R. Blick and S. H. Owades, *A.S.B.C. Proc.*, 1967, p. 75.
473 B. Paletta, *Mikrochim. Acta*, 6 (1969) 1210.
474 B. Paletta and K. Panzenbeck, *Clin. Chim. Acta*, 26 (1969) 11.
475 M. K. Pápay, K. Tóth and E. Pungor, *Anal. Chim. Acta*, 56 (1971) 291.
476 J. Papp and J. Havas, *Hung. Sci. Instrum.*, (1970) No. 17.
477 E. Papp and E. Pungor, *Z. Anal. Chem.*, 250 (1970) 31.
478 S. J. Patterson, N. G. Bunton and N. T. Crosby, *Water Treat. Exam.*, 18 (1969) 182.
479 J. L. Paul and R. M. Carlson, *J. Agr. Food Chem.*, 16 (1968) 766.
480 J. Pavel, R. Kuebler and H. Wagner, *Microchem. J.*, 15 (1970) 192.
481 J. S. Parsons, *Anal. Chem.*, 30 (1958) 1262.
482 C. J. Pedersen, *J. Amer. Chem. Soc.*, 89 (1967) 7017.
483 C. J. Pedersen, *J. Amer. Chem. Soc.*, 92 (1970) 386.
484 C. J. Pedersen, *J. Amer. Chem. Soc.*, 92 (1970) 391.
485 C. J. Pedersen and H. K. Frensdorff, *Angew. Chem.*, 84 (1972) 16.
486 G. A. Perley, *Anal. Chem.*, 21 (1949) 391.
487 A. D. Perris and J. F. Whitfield, *Nature*, 216 (1967) 1350.
488 A. D. Perris, J. F. Whitfield and P. K. Tolg, *Nature*, 219 (1968) 527.
489 M. H. Peters and D. M. Ladd, *Talanta*, 18 (1971) 665.
489a J. Petránek and O. Ryba, *Collect. Czech. Chem. Commun.*, in press.
490 Philips Analytical Equipment, *Philips Ion Selective Electrodes*, October 1970.

491 Philips Gloeilampenfabrieken, *Ion Selective Electrodes.*
492 Philips, *Ion-Selective, Solid-State Electrode for Fluoride, Type No.* 15 560-*F.*
493 Philips, *Ion-Selective, Solid-State Electrodes for Iodide, Bromide, Chloride and Cyanide, Type IS* 550.
494 Philips, *Ion-Selective Solid-State Electrode for Sulfide and Silver, Type IS* 550 *S/Ag.*
495 Philips, *Liquid Membrane Ammonium Electrode, Type No. IS* 560-NH_4.
496 Philips, *Liquid Membrane Calcium Electrode, Type No. IS* 560-*Ca.*
497 Philips, *Liquid Membrane Potassium Electrode, Type No. IS* 560-*K.*
498 C. S. G. Phillips and R. J. P. Williams, *Inorganic Chemistry*, Vol. 2, Oxford University Press, Oxford, 1966, p. 106.
498a M. Pinkerton, L. K. Steinrauf and P. Dawkins, *Biochem. Biophys. Res. Commun.*, 35 (1969) 512.
499 L. Pioda, *Zur Ionenspezifität von Antibiotika*, Thesis, ETH, Zürich, 1969, Juris Verlag, Zürich, 1969.
500 L. A. R. Pioda and W. Simon, *Chimia*, 23 (1969) 72.
501 L. A. R. Pioda, V. Stanková and W. Simon, *Anal. Lett.*, 2 (1969) 665.
502 L. A. R. Pioda, W. Simon, H.-R. Bosshard and H. Ch. Curtius, *Clin. Chim. Acta*, 29 (1970) 289.
503 L. A. R. Pioda, H. A. Wachter, R. E. Dohner and W. Simon, *Helv. Chim. Acta*, 50 (1967) 1373.
504 L. A. R. Pioda, H. K. Wipf and W. Simon, *Chim.*, 22 (1968) 184.
505 C. B. Pittinger, *Anesth. Analg.*, 49 (1970) 540.
506 C. B. Pittinger, *Chemical Rubber Company Crit. Rev. Clin. Lab. Sci.*, 1 (1970) 351.
507 M. Planck, *Ann. Phys. Chem. N.F.*, 39 (1890) 196.
508 M. Planck, *Ann. Phys. Chem. N.F.*, 40 (1890) 561.
509 P. A. Plattner, U. Nager and A. Baller, *Helv. Chim. Acta*, 31 (1948) 594.
510 C. E. Plucinski, *U. S. At. Energy Comm.*, BNWL-601, 1968.
511 S. Potterton and W. D. Shults, *Anal. Lett.*, 1 (1967) 11.
512 B. C. Pressman, *Antimicrob. Ag. Chemother.*, (1969) 28.
513 B. C. Pressman, *Fed. Proc.*, 27 (1968) 1283.
513a B. C. Pressman, in L. Bolis and B. A. Pethica, *Mode of Action of Transport-Mediating Antibiotics, Membrane Models and the Formation of Biological Membranes*, North Holland, Amsterdam, 1968, p. 258.
514 B. C. Pressman, *Proc. Natl. Acad. Sci.*, 53 (1965) 1076.
515 B. C. Pressman, E. J. Harris, W. S. Jager and J. H. Johnson, *Proc. Natl. Acad. Sci.*, 58 (1967) 1949.
516 J. H. Prestergard and S. I. Chan, *Biochem.*, 8 (1969) 3921.
517 J. H. Prestergard and S. I. Chan, *J. Amer. Chem. Soc.*, 92 (1970) 4440.
518 E. Pungor, *Anal. Chem.*, 39 (1967) 28A.
519 E. Pungor and J. Havas, *Acta Chim. Acad. Sci. Hung.*, 50 (1966) 77.
520 E. Pungor, J. Havas and K. Tóth, *Acta Chim. Acad. Sci. Hung.*, 41 (1964) 239.
521 E. Pungor, J. Havas and K. Tóth, *Acta Chim. Acad. Sci. Hung.*, 48 (1966) 17.
522 E. Pungor and E. Hallós-Rokosinyi, *Acta Chim. Acad. Sci. Hung.*, 27 (1961) 63.
523 E. Pungor, E. Schmidt and K. Tóth, *Proc. IMEKO Symposium on Electrochemical Sensors, Veszprém*, 1968, p. 121.
524 E. Pungor and K. Tóth, *Anal. Chim. Acta*, 47 (1969) 291.
525 E. Pungor and K. Tóth, *Analyst*, 95 (1970) 625.
526 E. Pungor and K. Tóth, *Hung. Sci. Instrum.*, (1970) No. 18.
527 E. Pungor, K. Tóth and J. Havas, *Hung. Sci. Instrum.*, (1965) No. 3.
528 R. A. Raby and W. E. Sunderland, *Anal. Chem.*, 39 (1967) 1304; see also correction: *Anal. Chem.*, 40 (1968) 939.
529 I. C. Radale, B. Hoffken, D. K. Parkinson, J. Sheepers and A. Lackham, *Clin. Chem.*, 17 (1971) 1002.
530 I. C. Radale, D. K. Parkinson, B. Hoffken, K. E. Appiah and W. B. Hanley, *Ann. R. Coll. Phys. Surg. Can.*, 3 (1970) 34.
531 Radelkis Electrochemical Instruments, *Ion-Selective Electrodes*, 1971.
532 Radiometer A.S., *Instructions for Bromide Selectrode, Type F* 1022 *Br.*
533 Radiometer A.S., *Instructions for Chloride Selectrode, Type F* 1012 *Cl.*
534 Radiometer A.S., *Instructions for Sodium Glass Electrode, Type G* 502 *Na.*
535 P. Rahlfs, *Z. Phys. Chem.*, B 31 (1936) 157.
536 A. Raman, *Biochem. Med.*, 3 (1970) 369.
537 G. A. Rechnitz, *Acc. Chem. Res.*, 3 (1970) 69.
538 G. A. Rechnitz, *Anal. Chem.*, 41 (1969) 109A.
539 G. A. Rechnitz, *Analytical Studies on Ion-Selective Electrodes*, Chapter 9 of ref. 288.

540 G. A. Rechnitz, *Chem. Eng. News*, 45 (1967) 146.
541 G. A. Rechnitz and T. M. Hseu, *Anal. Chem.*, 41 (1969) 111.
542 G. A. Rechnitz and N. C. Kenny, *Anal. Chem.*, 2 (1969) 395.
543 G. A. Rechnitz and N. C. Kenny, *Anal. Lett.*, 3 (1970) 509.
544 G. A. Rechnitz and M. R. Kresz, *Anal. Chem.*, 38 (1966) 1786.
545 G. A. Rechnitz, M. R. Kresz and S. B. Zamochnik, *Anal. Chem.*, 38 (1966) 973.
546 G. A. Rechnitz and Z. F. Lin, *Anal. Chem.*, 40 (1968) 696.
547 G. A. Rechnitz and Z. F. Lin, *Anal. Chem.*, 39 (1967) 1406.
548 G. A. Rechnitz and Z. F. Lin, *Anal. Lett.*, 1 (1967) 23.
549 G. A. Rechnitz, Z. F. Lin and S. B. Zamochnik, *Anal. Lett.*, 1 (1967) 29.
550 G. A. Rechnitz and R. A. Llenado, *Anal. Chem.*, 42 (1970) 1779.
550a G. A. Rechnitz and R. A. Llenado, *Anal. Chem.*, 43 (1971) 283.
551 G. A. Rechnitz and M. S. Mohan, *Science*, 168 (1970) 1460.
552 J. M. C. Ridden, R. R. Barefoot and J. G. Roy, *Anal. Chem.*, 43 (1971) 1109.
553 P. Rinaldo and P. Montesi, *Chim. Ind.*, 53 (1971) 26.
554 C. E. Robertson and J. D. Hem, *Geochim. Cosmochim. Acta*, 32 (1968) 1343.
555 C. E. Robertson and J. D. Hem, *Geological Survey, Water-Supply Paper* 1827-C, Superintendent of Documents, U.S. Government Printing Office, Washington, 1969.
556 W. G. Robertson and M. Peacock, *Clin. Chim. Acta*, 20 (1968) 315.
557 W. H. Robertson, *Clin. Chim. Acta*, 24 (1969) 149.
558 R. A. Robinson, W. C. Duer and R. G. Bates, *Anal. Chem.*, 43 (1971) 1862.
559 W. I. Rogers and J. Wilson, *Anal. Biochem.*, 32 (1969) 31.
560 J. W. Ross, *Pittsburgh Conf. Anal. Chem. Appl. Spectrosc., Cleveland, Ohio, March* 1968, Paper 112.
561 J. W. Ross, *Science*, 156 (1967) 1378.
562 J. W. Ross, *Solid-State and Liquid Membrane Ion-Selective Electrodes*, Chapter 2 of ref. 288.
563 J. W. Ross and M. S. Frant, *Anal. Chem.*, 41 (1969) 967.
564 J. W. Ross and M. S. Frant, *Anal. Chem.*, 41 (1969) 1900.
565 J. Růžička, *Proc. IVth Int. Symp. Microtechniques, Graz*, 1970, p. 227.
566 J. Růžička and C. G. Lamm, *Anal. Chim. Acta*, 54 (1971) 1.
567 J. Růžička and C. G. Lamm, *Anal. Chim. Acta*, 53 (1971) 206.
568 J. Růžička and K. Rald, *Anal. Chim. Acta*, 53 (1971) 1.
569 J. Růžička and J. C. Tjell, *Anal. Chim. Acta*, 47 (1969) 475.
570 J. Růžička and J. C. Tjell, *Anal. Chim. Acta*, 49 (1970) 346.
571 J. Růžička and J. C. Tjell, *Anal. Chim. Acta*, 51 (1970) 1.
571a J. A. Růžička and O. Zajíček, *Vod. Hospod.*, 19 (1969) 200.
572 C. Sachs, *Presse Med.*, 78 (1970) 1547.
573 C. Sachs, A. M. Bourdeau, M. Broyer and S. Balsan, *Ann. Biol. Clin.*, 28 (1970) 137.
574 R. Salomon, A. Sher and M. W. Müller, *J. Appl. Phys.*, 37 (1966) 3427.
575 J. P. Sandblom, *J. Phys. Chem.*, 73 (1969) 249.
576 J. P. Sandblom, G. Eisenman and J. L. Walker, *J. Phys. Chem.*, 71 (1967) 3862.
577 J. P. Sandblom, G.Eisenman and J. L. Walker, *J. Phys. Chem.*, 71 (1967) 3871.
578 H. Schiller, *Ann. Phys.*, 74 (1924) 105.
579 K. Schlyter, *Ark. Kem.*, 5 (1953) 61, 73.
580 R. Schlögl, *Z. Phys. Chem. N.F.*, 1 (1954) 305.
581 E. Schmidt and E. Pungor, *Anal. Lett.*, 4 (1971) 641.
582 R. P. Scholer and W. Simon, *Chim.*, 24 (1970) 372.
583 F. A. Schultz, *Anal. Chem.*, 43 (1971) 502.
584 F. A. Schultz, *Anal. Chem.*, 43 (1971) 1523.
585 F. A. Schultz, A. J. Petersen, C. A. Mask and R. P. Buck, *Science*, 162 (1968) 267.
586 K. Schwabe, *Fortschritte der pH-Messtechnik*, Berlin, 1958.
587 K. Schwabe and H. Dahms, *Z. Elektrochem.*, 65 (1961) 518.
588 K. Schwabe and H. D. Suschke, *Angew. Chem. Int. Ed. Engl.*, 3 (1964) 36.
589 R. Schwyzer, Aung Tun-Kyi, M. Caviezel and P. Moser, *Helv. Chim. Acta*, 53 (1970) 15.
590 P. Sekelj and R. B. Goldbloom, *Clinical Applications of Cation-Sensitive Glass Electrodes*, Chapter 19 of ref. 205.
591 W. Selig, *Microchem. J.*, 15 (1970) 452.
592 W. Selig, *Mikrochim. Acta*, 3 (1970) 229.

593 W. Selig, *Mikrochim. Acta*, 3 (1970) 564.
594 W. Selig, *Report No. UCOD*-15444, Lawrence Radiation Laboratory, University of California, Livermore, Calif., February 1969.
595 W. Selig, *Z. Anal. Chem.*, 249 (1970) 30.
596 N. Shane and D. Miele, *J. Pharm. Sci.*, 57 (1968) 1260.
597 A. Shatkay, *Anal. Chem.*, 39 (1967) 1056.
598 A. Shatkay, *Biophys. J.*, 8 (1968) 912.
599 A. Shatkay, *Talanta*, 17 (1970) 381.
600 A. Shatkay and A. Lerman, *Anal. Chem.*, 41 (1969) 514.
601 E. C. Shaw and P. Wiley, *Calif. Agr.*, 5 (1969) 11.
602 E. Shchari, J. Jagur-Grodzinski, Z. Luz and M. Shparer, *J. Amer. Chem. Soc.*, 93 (1971) 7133.
603 G. M. Shean and K. Sollner, *Ann. N.Y. Acad. Sci.*, 137 (1966) 759.
604 M. M. Shemyakin, *Angew. Chem.*, 72 (1960) 342.
605 M. M. Shemyakin, N. A. Aldanova, E. I. Vinogradova and M. J. Feigina, *Tetrahedron Lett.*, (1963) 1921.
606 M. M. Shemyakin, Yu. A. Ovchinnikov, V. T. Ivanov, V. K. Antonov, A. M. Shkrob, I. I. Mikhaleva, A. V. Yevstratov and G. G. Malenkov, *Biochem. Biophys. Res. Commun.*, 29 (1967) 834.
607 M. M. Shemyakin, Yu. A. Ovchinnikov, V. T. Ivanov, V. K. Antonov, E. I. Vinogradova, A. M. Shkrob, G. G. Malenkov, A. V. Yevstratov, I. A. Laine, J. I. Melnik and I. D. Ryabova, *J. Membrane Biol.*, 1 (1969) 402.
608 A. Sher, R. Solomon and K. Lee, *Phys. Rev.*, 144 (1966) 593.
609 H. E. Simmons and C. H. Park, *J. Amer. Chem. Soc.*, 90 (1968) 2431.
610 W. Simon, *Electrochem. Soc. Meet., New York, May* 1969.
611 W. Simon, H.-R. Wuhrmann, M. Vašák, L. A. R. Pioda, R. Dohner and Z. Štefanac, *Angew. Chem.*, 82 (1970) 433.
612 D. R. Simpson, *Amer. Mineral.*, 54 (1969) 1711.
613 L. Singer and W. D. Armstrong, *Anal. Chem.*, 40 (1968) 613.
614 L. Singer and W. D. Armstrong, *Arch. Oral Biol.*, 14 (1969) 1343.
615 L. Singer, W. D. Armstrong and J. J. Vogel, *J. Lab. Clin. Med.*, 74 (1969) 354.
616 M. J. Smith and S. E. Manahan, *Anal. Chim. Acta*, 48 (1969) 315.
617 S. I. Sokolov and A. H. Passynsky, *Z. Phys. Chem.*, A 160 (1932) 366.
618 K. Sollner, *Ann. N.Y. Acad. Sci.*, 148 (1968) 154.
619 K. Sollner, *J. Macromol. Sci. Chem.*, A 3 (1969) 1.
620 K. Sollner, *Z. Elektrochem.*, 36 (1930) 36.
621 K. Sollner and G. M. Shean, *J. Amer. Chem. Soc.*, 86 (1964) 1901.
622 K. Sollner and G. M. Shean, *Protoplasma*, 63 (1967) 174.
623 K. Srinivasan and G. A. Rechnitz, *Anal. Chem.*, 40 (1968) 509.
624 K. Srinivasan and G. A. Rechnitz, *Anal. Chem.*, 40 (1968) 1818.
625 K. Srinivasan and G. A. Rechnitz, *Anal. Chem.*, 40 (1968) 1955.
626 K. Srinivasan and G. A. Rechnitz, *Anal. Chem.*, 41 (1969) 1203.
626a R. H. Stokes and R. A. Robinson, *J. Amer. Chem. Soc.*, 70 (1948) 1870.
627 Z. Štefanac and W. Simon, *Chim.*, 20 (1966) 436.
628 Z. Štefanac and W. Simon, *Microchem. J.*, 12 (1967) 125.
629 L. K. Steinrauf, M. Pinkerton and J. W. Chamberlin, *Biochem. Biophys. Res. Commun.*, 33 (1968) 29.
629a L. Šůcha and M. Suchánek, *Anal. Lett.*, 3 (1970) 613.
629b L. Šůcha, M. Suchánek and Z. Urner, *Proc. 2nd Conf. Appl. Phys. Chem., Veszprém*, 1971, I, p. 651.
630 M. W. Sun, *Amer. Ind. Hyg. Assoc. J.*, 2 (1969) 133.
631 T. W. Swaddle and W. E. Jones, *Can. J. Chem.*, 48 (1970) 1054.
632 G. Szabó, G. Eisenman and S. Ciani, Ion Distribution Equilibria in Bulk Phases and the Ion Transport Properties in Lipid Bilayer Membranes Produced by Neutral Macrocyclic Antibiotics, *Proc. Coral Gables Conf. Physical Principles of Biological Membranes*, 1968, Gordon and Breach, New York, 1969.
633 G. Szabó, G. Eisenman and S. Ciani, *J. Membrane Biol.*, 1 (1969) 346.
634 S. L. Tackett, *Anal. Chem.*, 41 (1969) 1703.
635 K. K. Tanji, *Environ. Sci. Technol.*, 3 (1969) 656.
636 D. R. Taves, *Nature*, 217 (1968) 1050.
637 D. R. Taves, *Talanta*, 15 (1968) 1015.
638 H. J. C. Tendeloo and A. Krips, *Recl. Trav. Chim.*, 76 (1957) 703.
639 H. J. C. Tendeloo and A. Krips, *Recl. Trav. Chim.*, 78 (1959) 177.

640 T. Teorell, *Biophys. J.*, 2 No. 2, Pf. 2, Supplement 27 (1962).
641 T. Teorell, *Discuss. Faraday Soc.*, 21 (1956) 9.
642 T. Teorell, *Progr. Biophys. Biophys. Chem.*, 3 (1953) 300.
643 T. Teorell, *Trans. Faraday Soc.*, 33 (1937) 1053.
644 T. Teorell, *Z. Elektrochem.*, 55 (1951) 460.
644a L. M. Thomassen, T. Ellingsen and J. Ugelstad, *Acta Chem. Scand.*, 25 (1971) 3024.
645 M. E. Thompson, *Science*, 153 (1966) 867.
646 M. E. Thompson and J. W. Ross, *Science*, 154 (1966) 1643.
647 M. R. Thompson, *J. Res. Natl. Bur. Stand.*, 9 (1932) 833.
648 A. Thore, D. L. Keister, N. Shavit and A. San Pietro, *Biochem.*, 7 (1968) 3499.
649 O. Tomíček and R. Pulpán, *Collect. Czech. Chem. Commun.*, 11 (1956) 1444.
650 L. Torma and B. E. Ginther, *J. Ass. Offic. Agr. Chem.*, 51 (1968) 1181.
651 D. C. Tosteson, *Fed. Proc.*, 27 (1968) 1269.
652 D. C. Tosteson, T. E. Andreoli, M. Tieffenberg and P. Cook, *J. Gen. Physiol.*, 51 (1968) 373.
653 K. Tóth, I. Cavaller and E. Pungor, *Anal. Chim. Acta*, 57 (1971) 131.
654 K. Tóth and E. Pungor, *Anal. Chim. Acta*, 51 (1970) 221.
655 K. Tóth and E. Pungor, *Proc. IMEKO Symposium on Electrochemical Sensors, Veszprém, Hungary*, 1968, p. 35.
656 A. H. Truesdell and C. L. Christ, *Glass Electrodes for Calcium and Other Divalent Cations*, Chapter 11 of ref. 205.
657 A. H. Truesdell and A. M. Pommer, *Science*, 142 (1962) 1292.
658 M. R. Truter and D. Bright, *Nature*, 225 (1970) 176.
659 M. R. Truter and C. J. Pedersen, *Endeavour*, 30 (1971) 142.
660 J. Tušl, *Chem. Listy*, 64 (1970) 322.
661 J. Tušl, *Clin. Chim. Acta*, 27 (1970) 216.
662 J. Tušl, *J. Ass. Offic. Agr. Chem*., 53 (1970) 267.
663 R. W. Ure, *J. Chem. Phys.*, 26 (1957) 1363.
664 M. R. Urist, D. P. Speer, K. J. Ibsen and B. S. Strates, *Calcif. Tissue Res.*, 2 (1968) 253.
665 D. W. Urry, *Proc. Natl. Acad. Sci.*, 68 (1971) 672.
666 D. W. Urry, M. C. Goodall, J. D. Glickson and D. F. Mayers, *Proc. Natl. Acad. Sci.*, 68 (1971) 1907.
667 N. E. Vanderborgh, *Talanta*, 15 (1968) 1009.
668 J. C. Van Loon, *Anal. Chim. Acta*, 54 (1971) 23.
669 J. C. Van Loon, *Anal. Lett.*, 1 (1968) 393.
670 J. C. Van Loon, *Analyst*, 93 (1968) 788.
671 J. Veselý, private communication.
672 J. Veselý, *Chem. Listy*, 65 (1971) 86.
672a J. Veselý, *Collect. Czech. Chem. Commun.*, 36 (1971) 3365.
673 J. Veselý and J. Jindra, *Proc. IMEKO Symposium on Electrochemical Sensors, Veszprém*, 1968, p. 69.
674 P. Voogt, *Dtsch. Lebens.-Rundsch.*, 65 (1969) 196.
674a F. Vyskočil, N. Kříž and J. Bureš, *Brain Res.*, 39 (1972) 255.
675 H. Wada and Q. Fernando, *Anal. Chem.*, 43 (1971) 751.
676 C. Wagner, *J. Chem. Phys.*, 21 (1953) 1819.
677 J. L. Walker, *Anal. Chem.*, 43 (1971) 89A.
678 J. L. Walker, G. Eisenman and J. P. Sandblom, *J. Phys. Chem.*, 72 (1968) 978.
679 T. B. Warner, *Anal. Chem.*, 41 (1969) 527.
680 T. B. Warner, *Science*, 165 (1969) 178.
681 H. F. Wastgestian, *Z. Anal. Chem.*, 246 (1969) 237.
682 J. I. Watters, S. Kalliney and R. C. Machen, *J. Inorg. Nucl. Chem.*, 31 (1969) 3823.
683 C. W. Weber and B. L. Reid, *J. Nutr.*, 97 (1968) 90.
684 D. Weiss, *Chem. Listy*, 63 (1969) 1152.
685 D. Weiss, *Chem. Listy*, 65 (1971) 305.
686 D. Weiss, *Chem. Listy*, 65 (1971) 1071.
687 C. Westcott and F. Pearlman, *Beckman E. C. News*, 2 (1971) 3.
688 M. Whitfield and J. V. Leyendekkers, *Anal. Chem.*, 42 (1970) 444.
689 M. Whitfield and J. V. Leyendekkers, *Anal. Chim. Acta*, 45 (1969) 383.
690 M. Whitfield and J. V. Leyendekkers, *Anal. Chim. Acta*, 46 (1969) 63.
691 M. Whitfield, J. V. Leyendekkers and J. D. Kerr, *Anal. Chim. Acta*, 45 (1969) 399.

692 Th. Wieland, G. Lüben, H. Ottenheym, J. Faessel, J. X. de Vries, W. Konz, A. Prox and J. Schmid, *Angew. Chem.*, 80 (1968) 209.
693 L. M. Williams, *Tetracol*, 8 (1969) 41.
694 R. J. P. Williams, *J. Chem. Soc.*, (1952) 3770.
695 R. J. P. Williams, *Quart. Rev.*, 24 (1970) 331.
696 T. R. Williams, W. Boettner and S. Wakeham, *J. Chem. Educ.*, 47 (1970) 464.
697 H. K. Wipf, *Dissertation ETH*, Zürich, 1970.
698 H. K. Wipf, A. Olivier and W. Simon, *Helv. Chim. Acta*, 53 (1970) 1605.
699 H. K. Wipf, W. Pache, P. Jordan, H. Zähner, W. Keller-Schierlein and W. Simon, *Biochem. Biophys. Res. Commun.*, 36 (1969) 387.
700 H. K. Wipf, L. A. R. Pioda, Z. Štefanac and W. Simon, *Helv. Chim. Acta*, 51 (1968) 377.
701 H. K. Wipf and W. Simon, *Biochem. Biophys. Res. Commun.*, 34 (1969) 707.
702 H. K. Wipf and W. Simon, *Helv. Chim. Acta*, 53 (1970) 1732.
703 M. M. Wise, M. J. Kurey and G. Baum, *Clin. Chem.*, 16 (1970) 103.
703a K. H. Wong, G. Konizer and J. Smid, *J. Amer. Chem. Soc.*, 92 (1970) 666.
704 J. H. Woodson and H. A. Liebhafsky, *Anal. Chem.*, 41 (1969) 1894.
705 J. H. Woodson and H. A. Liebhafsky, *Nature*, 224 (1969) 690.
706 C. Woodward and E. A. Davidson, *Proc. N.A.S.*, 60 (1968) 201.
707 E. A. Woolson, J. H. Axley and P. C. Kearney, *Soil Sci.*, 109 (1970) 270.
708 D. Woorman, K. F. Bonnhoeffer and N. Helfferich, *Z. Phys. Chem. N.F.*, 8 (1956) 265.
709 M. R. Wyllie and H. W. Patnode, *J. Phys. Chem.*, 54 (1950) 204.
710 R. S. Yunghans and T. B. McMuller, *Fluoride*, 3 (1970) 143.
711 W. H. Zachariasen, *J. Amer, Chem. Soc.*, 54 (1932) 3841.
712 A. Zalkin and D. H. Templeton, *J. Amer. Chem. Soc.*, 75 (1953) 2453.
713 W. Simon, private communication.

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SPECTROPHOTOMETRIC DETERMINATION OF ANTIMONY IN SEBACATE-BASE LUBRICANTS BY THE IODIDE METHOD

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The determination of antimony in lubricants is important because antimony compounds, such as triphenylstibine[1], alkyl compounds of antimony[2], bis(4-*tert.*-butylpyrocatechol)-antimonite[3], tris(4-*tert.*-butylpyrocatechol) antimonate[3], antimony dialkyldithiocarbamates[4,5], antimony dialkylphosphorodithioates[4,5], and antimony trichloride[6] are used as additives in petroleum-base and synthetic lubricants.

Apparently, there is little in the literature on the determination of antimony in lubricants. However, methods have been described for the determination of antimony in organic compounds by titration[7,8], spectrophotometrically by the rhodamine β color[9,10], and spectrophotometrically by the color formed with a potassium iodide–ascorbic acid reagent[11,12].

This laboratory undertook the development of a spectrophotometric method for the determination of antimony in sebacate-base lubricants. Attention was concentrated on the iodide method since the rhodamine method was found to be troublesome.

The use of potassium iodide for the spectrophotometric determination of antimony was apparently first proposed by Fauchon[13]. Subsequent investigators recommended adding a reducing agent with the potassium iodide in order to destroy iodine formed by air oxidation or by reaction of the antimony(V) with the potassium iodide. Ascorbic acid is the reducing agent most frequently used for this purpose[10–16]. Some investigators have used sodium hypophosphite. This reagent is preferred by the present authors (one advantage of sodium hypophosphite is that its cost is a fraction of that of ascorbic acid).

The use of sodium hypophosphite with potassium iodide in the determination of antimony was first proposed by Sandell in a semimicro procedure in the first edition of his book *Colorimetric Determination of Traces of Metals*[17]. (In the second and third editions of this book[10,18] Sandell recommends a procedure that uses ascorbic acid in preference to the sodium hypophosphite.) Subsequent investigators applied the potassium iodide–sodium hypophosphite reagent to the determination of antimony in the following metals: copper-base alloys (after separating the antimony by precipitation with metastannic acid)[19,20], tin (after separating the antimony by deposition on copper foil)[21], cast iron (after separating the antimony by precipitation with manganese dioxide)[22], and gold alloys[23].

EXPERIMENTAL

Reagents and apparatus

Potassium iodide–sodium hypophosphite reagent. Dissolve 125 g of potassium iodide and 50 g of sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$) in about 400 ml of water and dilute to 500 ml.

Standard antimony solution (1 ml = 0.10 mg of Sb). Transfer 0.1000 g of antimony metal to a 100-ml beaker, add 20 ml of sulfuric acid (s.g. 1.84), and heat until the antimony is dissolved. Cool, transfer to a 1-l volumetric flask with 10% sulfuric acid, cool again, and dilute to the mark with 10% sulfuric acid.

Spectrophotometer (Beckman Model B or equivalent).

Preparation of calibration curve

Transfer 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the standard antimony solution to 25-ml volumetric flasks and add 3.5 ml of sulfuric acid (s.g. 1.84). Dilute to about 10 ml with water and cool to about 15°. Add 10.0 ml of potassium iodide–sodium hypophosphite reagent and dilute to the mark with water. Measure the absorbance at 425 nm in 10–60 min against dilute sulfuric acid solution (3 ml of sulfuric acid per 25 ml). Plot absorbance against mg of antimony per 25 ml.

Procedure

For 0.00–0.05% *antimony.* Transfer a 2.5-g sample to a 250-ml beaker and add 9 ml of sulfuric acid (s.g. 1.84) and 25 ml of nitric acid (s.g. 1.42). Cover with a watch glass and evaporate to fumes of sulfur trioxide. Add nitric acid dropwise to the fuming solution until the solution is practically colorless. Allow to cool, wash down the watch glass and sides of the beaker, and evaporate to fumes of sulfuric acid without a watch glass. Compare the volume of the solution to 8 ml of water contained in a 250-ml beaker and adjust to about 8 ml either by further fuming or by the addition of sulfuric acid. Allow to cool, add about 60 ml of water, and boil down to about 30 ml. Allow to stand for about 1 h at room temperature. Filter through a Whatman No. 42 filter paper into a 250-ml beaker and wash with hot water. Boil down to 15–20 ml and cool. Transfer to a 25-ml volumetric flask with water and dilute to the mark.

Pipet two 10-ml aliquots into 25-ml volumetric flasks (it may be necessary first to decant the solution into a dry 30- or 50-ml beaker since some 10-ml pipets do not fit into 25-ml volumetric flasks). Cool to about 15°. Dilute one aliquot to the mark with water and use this sample as the blank. Add 10.0 ml of potassium iodide–sodium hypophosphite reagent to the second aliquot and dilute to the mark with water. Measure the absorbance of the second portion at 425 nm in 10–60 min against the blank. Convert the reading to mg of antimony by referring to the calibration curve. Calculate the percent antimony as follows:

$$\%\,\mathrm{Sb} = \frac{\text{mg of Sb as read from curve}}{\text{g of sample in aliquot} \cdot 10}$$

For 0.05–0.1% *antimony.* Proceed as for 0.00–0.05% antimony but use a 1.25-g sample.

For 0.1–0.2% *antimony.* Proceed as described for 0.00–0.05% antimony but use a 1.25-g sample. Pipet two 10-ml aliquots into 50-ml volumetric flasks, add 15 ml of water and 3 ml of sulfuric acid, and cool to about 15°. Develop the color and measure the absorbance as described for 0.00–0.05% antimony but use 20.0 ml of potassium iodide–sodium hypophosphite reagent and dilute to 50 ml. Multiply the percent antimony (calculated from the equation) by two.

DISCUSSION AND RESULTS

Effect of concentration of potassium iodide and sodium hypophosphite

The concentrations of potassium iodide and sodium hypophosphite recommended by previous investigators are summarized in Table I. It is seen that the potassium iodide concentration varied from 20.0 to 28.6%, the sodium hypophosphite concentration from 2.9 to 5.6%, and the ratio of potassium iodide to sodium hypophosphite from 9.9/1 to 5.0/1.

TABLE I

POTASSIUM IODIDE AND SODIUM HYPOPHOSPHITE CONCENTRATIONS USED BY PREVIOUS INVESTIGATORS

Investigator	*Potassium iodide concentration (%)*	*Sodium hypophosphite concentration (%)*	*Ratio of potassium iodide concentration to sodium hypophosphite concentration*
Sandell[17]	28.6	2.9	9.9/1
Holler[19]	20.0	4.0	5.0/1
Coppins and Price[21]	20.0	4.0	5.0/1
Rooney[22]	20.0	4.0	5.0/1
Yurash[23]	27.8	5.6	5.0/1
ASTM[20]	20.0	4.0	5.0/1

Attempts were made to apply the above conditions for using the potassium iodide–sodium hypophosphite method to the determination of antimony in sebacate-base lubricants after first destroying the organic matter by treatment with a mixture of sulfuric and nitric acids and evaporation to fumes of sulfuric acid. The attempts were unsuccessful since it was found that there was delayed release of iodine a few minutes after adding the potassium iodide–sodium hypophosphite reagent.

The release of iodine by air oxidation or by the presence of such metals as copper has been noted by previous investigators of the potassium iodide–sodium hypophosphite reagent. To eliminate this release of iodine, Holler[19] and Rooney[22] recommended the addition of sodium thiosulfate solution after the potassium iodide–sodium hypophosphite reagent. ASTM[20] recommended the addition of 25 mg of ascorbic acid for the same purpose. ASTM[20] states that the error from air oxidation can be minimized by not mixing the solution for 10 min after transferring it to the absorption cell.

Application of the above techniques did not eliminate the release of iodine in the determination of antimony in lubricants. Therefore, a different method of approach was considered. It was theorized that the release of iodine could be due to the concentrations of potassium iodide and sodium hypophosphite (and their ratios) not being optimal. It would seem that if the potassium iodide concentration were at a minimum and the sodium hypophosphite were adequately high, the sodium hypophosphite alone (in an acidic solution) would react with the free iodine completely.

The potassium iodide–sodium hypophosphite reagent finally selected contained 125 g of potassium iodide and 50 g of sodium hypophosphite per 500 ml. To test the effect of different amounts of this reagent, varying amounts were added to volumetric flasks containing 3.0 ml of sulfuric acid and 0.2 mg of antimony, the volumes were brought up to 25 ml, and the color was measured at 425 nm with a Beckman Model B Spectrophotometer. The results (Table II) showed that the color leveled off at about 10.0 ml of the reagent and this is the amount of reagent recommended. When this amount of the reagent is used, the concentrations of the potassium iodide and sodium hypophosphite in the 25-ml volume in which the color is developed are 10.0% and 4.0%, respectively. The ratio of potassium iodide concentration to sodium hypophosphite concentration is 2.5/1.

The reagent recommended remains colorless for a month.

TABLE II

EFFECT OF AMOUNT OF POTASSIUM IODIDE–SODIUM HYPOPHOSPHITE REAGENT (per 25 ml)

Reagent (ml)	2.0	5.0	10.0	12.0	13.0
%T	61	55	53	52	52

Effect of acidity

In the study of the effect of acidity, sulfuric acid was the only acid tested since this is the only acid finally present. Solutions containing 0.2 mg of antimony and varying amounts of sulfuric acid from 0.2 to 6.0 ml were treated with 10.0 ml of potassium iodide–sodium hypophosphite solution and the volumes were brought up to 25 ml. The results showed that the color was the same over the range 1.0–5.0 ml of sulfuric acid per 25 ml. The use of 3.0 to 3.5 ml of sulfuric acid per 25 ml is recommended. Transmittance increased with less than 1.0 ml of sulfuric acid, and a dark brown color appeared with 6.0 ml of sulfuric acid.

Effect of temperature

For best results the temperature should be between 15° and 18°. To attain this temperature it is necessary to cool the solution before adding the potassium iodide–sodium hypophosphite reagent.

Stability of the color

The color developed in 10 min, remained unchanged for 1 h, and then showed slight changes over the interval 1–7 h. It is recommended that the color be measured in 10–60 min.

Absorption spectra

Absorption spectra obtained for 0.1, 0.3, and 0.5 mg of antimony per 25 ml and for the blank (all against distilled water), with a Cary Model 15 recording spectro-

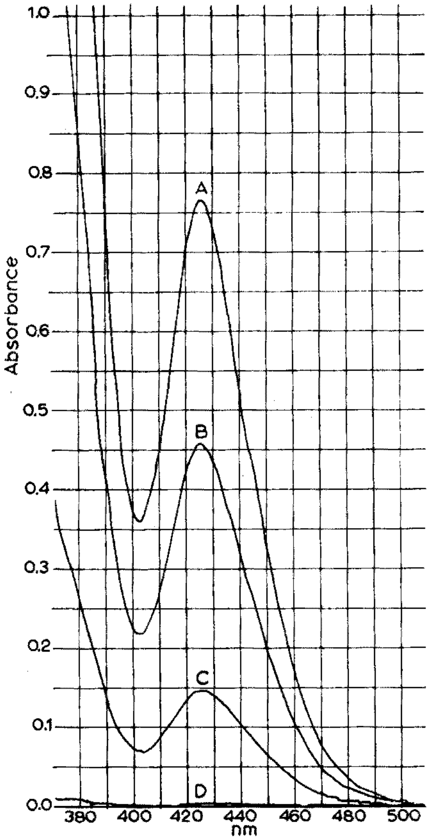

Fig. 1. Absorbance spectra for antimony iodide color. (A) 0.5 mg, (B) 0.3 mg, (C) 0.1 mg Sb per 25 ml, (D) blank.

photometer are shown in Fig. 1. It is seen that maximum absorbance occurs at 425 nm and the wavelength does not change with concentration of the antimony. The blank showed no significant absorbance at 425 nm.

Range

The recommended range of the method is 0–0.5 mg of antimony per 25 ml. This would be equivalent to 0.00–0.05% antimony on a 1-g sample and 0.05–0.1% antimony on a 0.5-g sample. For 0.1–0.2% antimony, a 0.5-g sample is diluted to 50 ml after adding 20 ml of potassium iodide–sodium hypophosphite reagent.

Blank

On destroying the organic matter by treatment with a mixture of sulfuric and nitric acids and evaporation to fumes of sulfuric acid, the solution is ordinarily colorless. However, at times a sample solution may be encountered that has a faint yellow tinge. It is essential, therefore, in order to eliminate any error due to the absorbance of the sample to take one aliquot for a blank and a second aliquot for developing the iodide color. The aliquots should not be heated (to reduce the volume) since this may affect their color.

The blank as run above does not correct for the absorbance of the potassium iodide–sodium hypophosphite reagent. However, this absorbance was always found to be insignificant in acid solution.

Effect of valence of antimony

The same rectilinear calibration curves were obtained with antimony(III) and antimony(V) solutions (for a Beckman Model B Spectrophotometer). The antimony(III) solutions were prepared by two means: (*a*) dissolution of antimony metal in concentrated sulfuric acid and dilution, (*b*) dissolution of potassium antimonyl tartrate in dilute sulfuric acid. The antimony(V) solutions were prepared by treating aliquots of the sulfuric acid solution of the antimony metal with a few drops of perchloric acid and evaporating to strong fumes. Of course, antimony(V) is reduced instantaneously to antimony(III) by the hypophosphite. Apparently, antimony(V) iodide cannot exist in aqueous solution; in fact, Payne[24] questions that it can exist at all.

Interferences

Many synthetic lubricants contain barium sulfonate which is converted to barium sulfate on fuming with sulfuric acid. In the proposed method the barium sulfate was filtered off, after first boiling the solution for several minutes to eliminate occlusion of antimony. Silica and lead sulfate would be filtered off with the antimony; however, silicon and lead are usually not found in synthetic lubricants.

The use of a mixture of perchloric, sulfuric, and nitric acids to destroy the organic matter is not recommended because perchloric acid not driven off during the fuming will subsequently precipitate as potassium perchlorate on addition of the potassium iodide–sodium hypophosphite reagent.

Comprehensive studies of interferences with the iodide method for antimony have been made by previous investigators[10,11,15,16,19]. No constituent of lubricants would be expected to interfere.

Results for antimony in sebacate-base lubricants

Seven samples of sebacate-base lubricants were analysed for antimony. Six of these samples were found to contain no antimony at all. The other sample was analysed six times, the average result being 0.19% antimony (error 0.01%). The presence of antimony in this sample and its absence in the remaining samples were confirmed spectrographically. It is believed that the antimony is present as an antimony dialkyldithiocarbamate, or an antimony dialkylphosphorodithioate. These compounds have an antimony content of 10–16%. Therefore, 0.19% of antimony would be equivalent to 1.2–1.9% of the compounds. All the lubricants tested were supposedly of the MIL-L-46000B[25] type and should not contain antimony.

The recoveries obtained on adding aliquots of standard antimony solution to portions of antimony-free lubricant (one of the above samples) and carrying the samples through the procedure were entirely satisfactory.

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SUMMARY

A spectrophotometric method is proposed for the determination of antimony in sebacate-base lubricants by means of the yellow complex obtained with a potassium iodide–sodium hypophosphite reagent. Organic matter is destroyed by treatment with a mixture of sulfuric and nitric acids and evaporation to fumes of sulfuric acid. Barium sulfate is filtered off, the solution is diluted in a volumetric flask, one aliquot is taken for the blank, and another aliquot is taken for development of the color. Various factors affecting the development of the color were studied.

RÉSUMÉ

On propose une méthode spectrophotométrique pour le dosage de l'antimoine dans des lubrifiants à base de sébaçate, en utilisant le complexe jaune formé avec le réactif: iodure de potassium–hypophosphite de sodium. La substance organique est détruite par traitement sulfonitrique et évaporation jusqu'aux fumées d'acide sulfurique. Divers paramètres pouvant affecter la coloration sont examinés.

ZUSAMMENFASSUNG

Für die Bestimmung von Antimon in Sebacat-Schmierstoffen wird eine spektrophotometrische Methode vorgeschlagen, die auf der Bildung eines gelben Komplexes mit einem Kaliumjodid–Natriumhypophosphit-Reagenz beruht. Organische Substanz wird durch Behandlung mit einem Gemisch von Schwefelsäure und Salpetersäure und durch Eindampfen bis zum Rauchen der Schwefelsäure zerstört. Bariumsulfat wird abfiltriert, die Lösung auf ein bestimmtes Volumen verdünnt und ein aliquoter Anteil als Vergleichslösung und ein anderer für die Entwicklung der Färbung verwendet. Verschiedene Faktoren, die die Farbentwicklung beeinflussen, wurden untersucht.

REFERENCES

1 R. Rosen (Standard Oil Development Co.), *U.S. Patent* 2, 181, 913, December 5, 1939.
2 R. Rosen (Standard Oil Development Co.), *U.S. Patent* 2, 181, 915, December 5, 1939.
3 O. L. Harle and J. R. Thomas (Calif. Research Corp.), *U.S. Patent* 2, 795, 551, June 11, 1957.
4 H. H. Farmer, B. W. Malone and H. F. Tompkins (R. T. Vanderbilt Co.), *Lubric. Eng.*, 23, No. 2 (1967) 57.
5 R. T. Vanderbilt Co., *Netherlands Patent Appl.* 302, 130, October 11, 1965.
6 H. Lepp, *French Patent* 988, 922, September 3, 1951.
7 N. T. Wilkinson, *Analyst*, 78 (1953) 165.
8 G. Bähr, H. Bieling and K. H. Thiele, *Z. Anal. Chem.*, 145 (1955) 105.
9 T. H. Maren, *Anal. Chem.*, 19 (1947) 487.
10 E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Ed., Interscience, New York, 1959, p. 266.
11 E. W. McChesney, *Ind. Eng. Chem., Anal. Ed.*, 18 (1946) 146.
12 P. F. Wyatt, *Analyst*, 80 (1955) 368.
13 L. Fauchon, *J. Pharm. Chim.*, 25 (1937) 537.
14 J. Bassett and J. C. H. Jones, *Analyst*, 91 (1966) 176.
15 D. Blazejak-Ditges and H. Klingeleers, *Z. Anal. Chem.*, 248 (1969) 18.

16 A. Elkind, K. H. Gayer and D. F. Boltz, *Anal. Chem.*, 25 (1953) 1744.
17 E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 1st Ed., Interscience, New York, 1944, p. 131.
18 E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 2nd Ed., 1950, p. 167.
19 A. C. Holler, *Anal. Chem.*, 19 (1947) 353.
20 American Soc. for Testing and Materials, 1971 *Annual Book of ASTM Standards. Part 32. Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores*, Philadelphia, Pa., 1971, p. 418.
21 W. C. Coppins and J. W. Price, *Metallorgia*, 46 (1952) 52.
22 R. C. Rooney, *Analyst*, 82 (1957) 619.
23 B. Yurash, *Chemist-Analyst*, 56, 1–2 (1967) 28.
24 D. S. Payne, *Quart. Rev. Chem. Soc.*, 15 (1961) 173.
25 *Military Specification, Lubricating Oil, Semi-Fluid (Automatic Weapons), MIL*-46000*B*, March 1970.

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NEUTRON-CAPTURE GAMMA-RAY STUDIES OF MARINE MANGANESE NODULES USING A NUCLEAR REACTOR AND A CALIFORNIUM-252 SOURCE

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Recently, success in the marine recovery of petroleum sulfur and magnetite has led to interest in the ocean floor as a source of metals[1]. The discovery of ferromanganese oxides, called manganese nodules, in large areas of the ocean and in the Great Lakes, has attracted industrial interest[2].

The work described in this paper was directed to the development of a possible neutron activation analysis for the detection of manganese on the ocean floor. It was found that neutron capture γ-rays characteristic of the manganese can be used; results obtained with neutrons from a reactor and from a californium-252 source are discussed.

REACTOR STUDY

A neutron beam at $2 \cdot 10^6$ n cm^{-2} s^{-1}, from the graphite thermal column of the University of Maryland 10-kW pool reactor (UMR) was used for 40-min irradiation of both pure manganese dioxide (203 g) and a crushed marine manganese nodule (31.7 g) from the Pacific Ocean.

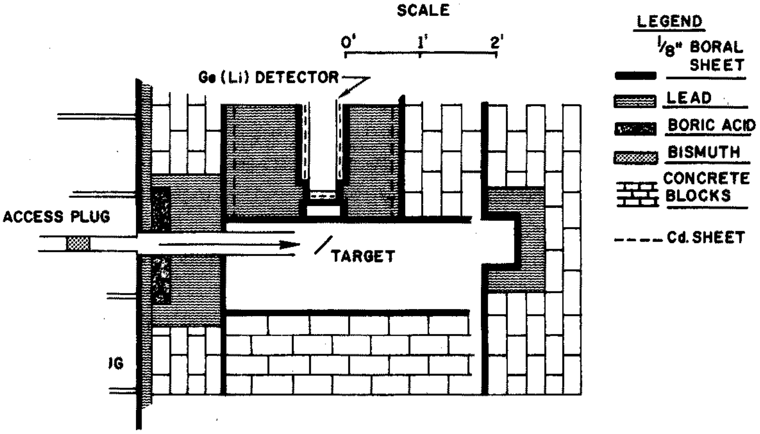
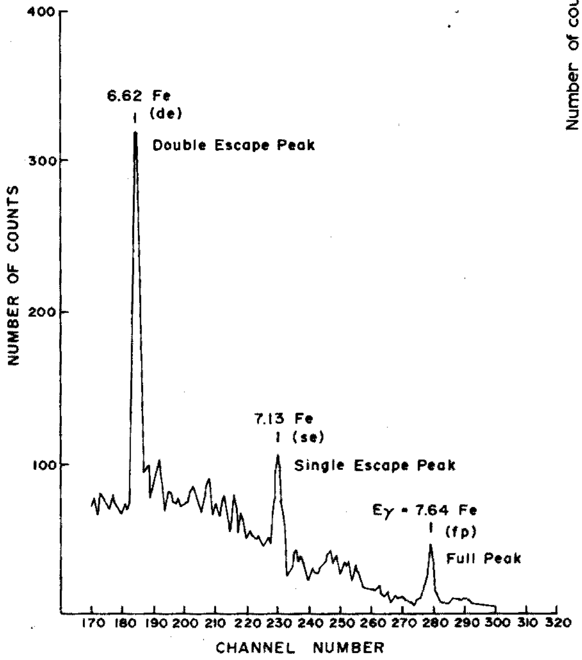


Fig. 1. University of Maryland reactor—external shield and detector geometry.

A 50-cm^3 lithium-drifted germanium, Ge(Li), γ-ray detector in a cavity shielded with lead and boron was placed near the sample (Fig. 1). The output signals from the detector went to a 1024-channel pulse-height analyzer. The energy range of the γ-rays in this study was 4.5–8.5 MeV. Both or one of the annihilation photons (0.511 MeV) from pair production, which is the predominant γ-ray process at this high energy, could escape the detecting region of the germanium crystal and produced double or single escape energy lines in the direct spectrum. Therefore, for a photon of high energy, lines were produced at $E_\gamma - 1.022$ (double escape (d)), a weaker one at $E_\gamma - 0.511$ MeV (single escape (s)) and the full energy peak (f). Figure 2 illustrates this multiple response from the 7.64-MeV iron capture γ-ray. These multiple peaks can be of advantage if there are interferences with some peaks from other constituents.



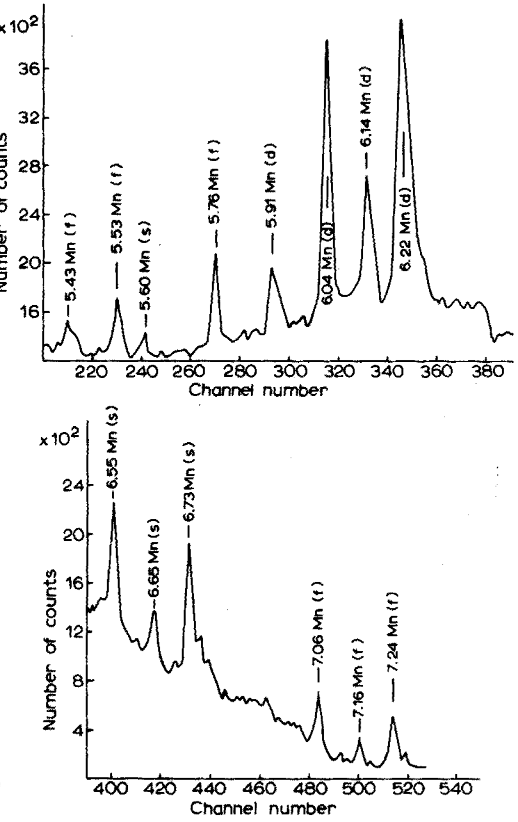


Fig. 2. Neutron capture γ-ray response of iron oxide sample.

Fig. 3. Neutron capture γ-ray response of pure manganese dioxide sample-reactor study.

Figure 3 shows the capture γ-ray spectrum for the pure manganese dioxide sample. The full, single, and double escape peaks agreed in energy and relative intensity with published values[3,5,6] (Table I). The trio of full energy peaks at 7.24, 7.16 and 7.06 MeV, the single escape peaks at 6.73, 6.65 and 6.55 MeV, and the relatively large double escape peaks at 6.22, 6.14 and 6.04 MeV should be noted. Tests on

TABLE I

HIGH-ENERGY CAPTURE γ-RAYS OF MANGANESE

Present work	*Rasmussen et al.*[3] *(Reactor)*		*Bartholomew and Kinsey*[6] *(Reactor)*		*Groshev et al.*[5] *(Reactor)*	
Energy (MeV)	*Energy (MeV)*	I^b	*Energy (MeV)*	*I*	*Energy (MeV)*	*I*
7.24 (f)	7.243	12.05	7.261	11.0	7.26	12.3
7.16 (f)	7.159	6.06	7.15	3.5	7.15	5.5
7.06 (f)	7.057	11.35	7.048	5.0	7.04	9.1
6.73 (s)	(6.73)[a]		(6.751)		(6.751)	
6.65 (s)	(6.649)		(6.64)		(6.64)	
6.55 (s)	(6.547)		(6.538)		(6.53)	
6.22 (d)	(6.223)		(6.241)		(6.24)	
6.14 (d)	(6.139)		(6.13)		(6.13)	
6.04 (d)	(6.037)		(6.028)		(6.02)	
5.91 (d) (f)	5.921	1.01	5.91	0.5	5.92	0.8
5.76 (f)	5.761	1.61	5.77	1.0	5.76	1.7
5.43 (f)	5.435	2.09				

[a] Numbers in parentheses are the single (s) and double (d) escapes of published full energy peaks.
[b] *I* is number of γ-rays per 100 neutrons captured.

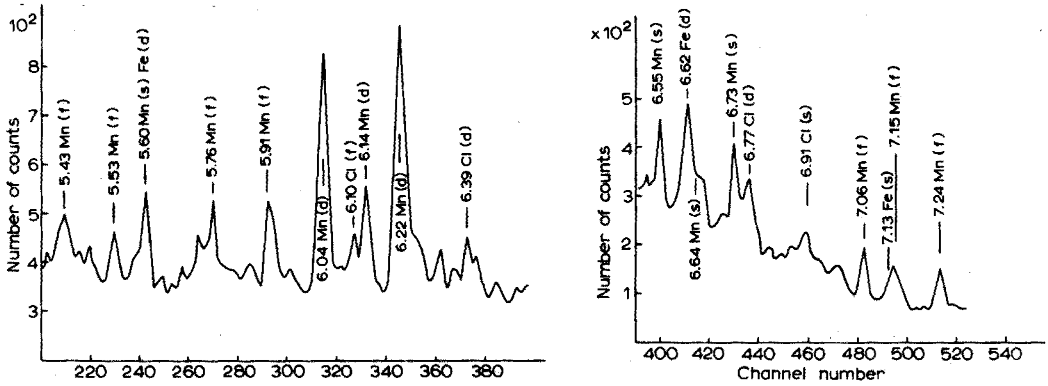


Fig. 4. Neutron capture γ-ray response of crushed manganese nodule-reactor study.

other elements, comparing a metal and its oxide, have shown oxygen to give no particular contribution to the spectrum during reactor activation[7].

Figure 4 shows the prompt γ-ray response for the crushed manganese nodule. This nodule, from the Lamont-Doherty Geological Observatory of Columbia University, was collected at *ca.* 2440 fathoms by the R.S.VEMA on cruise No. 20 on 10 April 1964 at latitude 14°25′N and longitude 145°52′ W[8]. Manganese nodules have been reported to contain 8–77% manganese, 2–26% iron, 1–20% silicon, 1–7% aluminum, and smaller percentages of copper, cobalt and nickel[9]. The γ-ray energies of the nodule sample corresponded to the capture γ-rays of pure manganese (Fig. 3). However, the relative peak heights of the full, single and double escape peaks were not the same. The difference was explained by the iron and copper in the nodule and residual salt from the sea. The strong 6.62-MeV iron and copper lines (double escape)

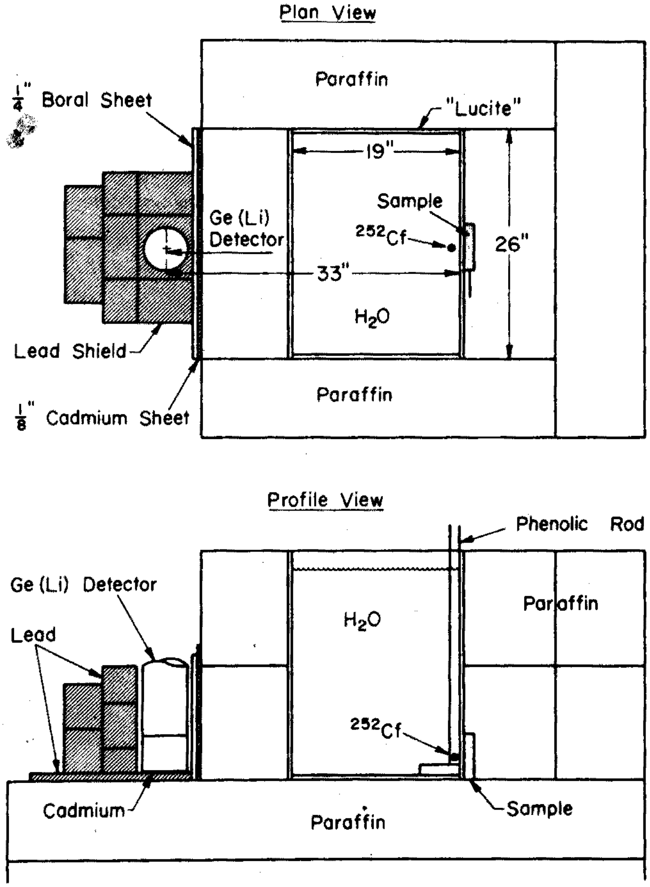


Fig. 5. Californium-252 experimental arrangement.

and the lines at 7.13 MeV (single escape) overshadowed the 6.65-MeV and 7.15-MeV manganese peaks (Fig. 2). Chlorine peaks, presumably from retained sea salt, appeared at 6.91 (s) 6.77 (d) 6.63 (f), 6.39 (d), and 6.10 (f) MeV.

CALIFORNIUM-252 STUDY

The californium-252 source used was initially 135 μg, but about 120 μg at the time of the experiment, and yielded $3 \cdot 10^8$ ns^{-1}. The californium in the form of an oxide (Cf_2O_3) coprecipitated with iron(III) oxide[10] was contained in a platinum shield which was doubly enclosed in a stainless steel capsule (type 304L; 0.37 in. diameter by 0.53 in. long). This capsule was held in a 3-ft. Micarta rod (1.5 in. diameter). The relatively long half-life (*ca.* 2.6 y) of californium-252 coupled with the high yield of neutrons distinguishes it from other isotopic sources. The neutron yields of 1-Curie isotopic neutron sources have been compared by Reinig and Evans[11]. These characteristics and ease in using californium-252 have made it attractive for laboratory and field use.

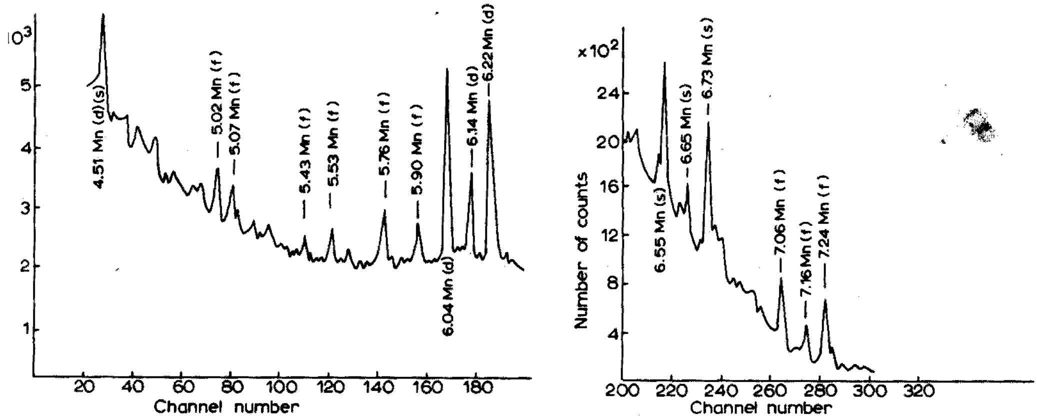


Fig. 6. Neutron capture γ-ray response of pure manganese dioxide sample—^{252}Cf study.

A pure manganese dioxide sample of 851 g was irradiated for 200 min in the californium-252 experiment arrangement (Fig. 5). A 30-cm^3 Ge(Li) detector observed the prompt photons. The output signals from the detector were fed to a 400-channel pulse-height analyzer. The trio of manganese full peaks at 7.24 MeV, 7.16 MeV and 7.06 MeV is seen in Fig. 6. The corresponding single escape peaks at 6.73 MeV, 6.65 MeV and 6.55 MeV and the double escape peaks at 6.22 MeV, 6.14 MeV and 6.04 MeV are clearly seen. These peaks have in general the same energy level and relative intensity as the pure manganese sample used in the reactor study. However, the 6.04 MeV (d), and presumably the 6.55 (s) and 7.06 (f) peaks are slightly higher than those of the reactor study. This could be due to the slightly higher-energy neutrons produced from the ^{252}Cf source.

A 300-g sample, taken from the same manganese nodule as that used in the UMR reactor study, was irradiated for 200 min by the ^{252}Cf source. Figure 7 shows the full peaks of manganese at 7.24 MeV, 7.16 MeV, and 7.06 MeV, the single escape peaks at 6.73 MeV, 6.55 MeV and 6.55 MeV, and the double escape peaks at 6.22 MeV, 6.14 MeV and 6.04 MeV. These energy lines agree with the pure MnO_2 results (Fig. 6). The 7.64 MeV, 7.13 MeV and 6.62 MeV sequence of iron is clear. Further iron peaks are evident, *i.e.* 8.27 MeV and 4.90 MeV, which are double escape peaks. The chlorine lines at 6.77 MeV and 6.11 MeV are also apparent. Nickel capture γ-peaks are seen at 8.49 MeV (single escape) and at 7.98 MeV (double escape). The nickel in the source capsule contributed to these nickel peaks.

Table II compares the number of counts in a specific capture γ-energy line of the pure manganese dioxide sample and the marine sample. After the counts had been corrected for weight, the precentage of manganese in the nodule was calculated. The percentage of manganese in the nodules obtained in the UMR and ^{252}Cf studies was essentially the same.

SIMULATED MARINE ENVIRONMENT STUDIES

Sea water

To simulate an ocean bottom environment, the lucite tank (26 × 19 × 22 in. as shown in Fig. 5) was filled with sea water. The californium-252 source was lowered

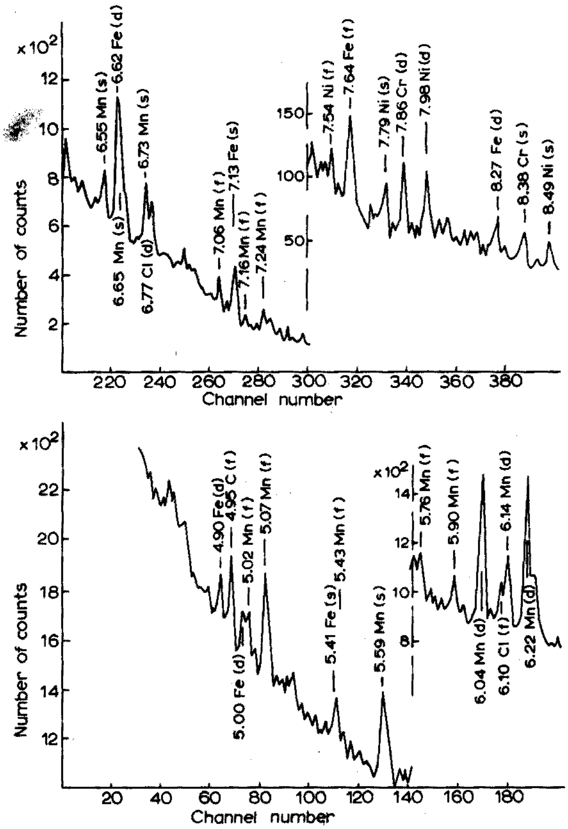


Fig. 7. Neutron capture γ-ray response of crushed manganese nodule sample—^{252}Cf study.

TABLE II

PERCENTAGE MANGANESE IN MARINE MANGANESE NODULE

Peak energy	*Counts MnO_2*	*Counts nodule*	*% Mn (nodule)*
UMR reactor study			
6.04	3821	832	40.7
6.14	2723	569	40.1
6.22	4136	887	40.7
		Ave.	40.5
^{252}Cf study			
6.04	5215	1485	38.2
6.14	3581	1157	43.0
6.22	4673	1475	42.0
		Ave.	41.06

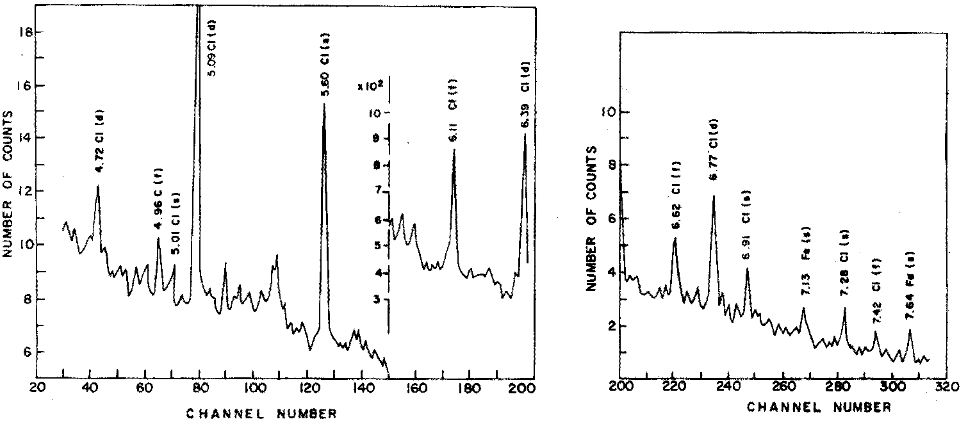


Fig. 8. Neutron capture γ-ray response of sea water.

into the water. After a capture γ-spectrum had been taken, approximately 3 in. of silica sand was spread evenly on the bottom of the tank. The Ge(Li) detector was placed outside the tank in the same position as in the previous ^{252}Cf studies.

This experimental arrangement was similar to a possible *in situ* exploration unit which could either be lowered from a mineral exploration research ship or carried by a deep diving research submarine[12]

Figure 8 shows the capture γ-spectrum obtained from a 40-min irradiation. The full peaks of chlorine at 7.42 MeV, 6.62 MeV and 6.11 MeV are easily identified. The single escape peaks at 7.28 MeV, 6.91 MeV, 5.60 MeV, and 5.01 MeV, and the double escape peaks at 6.77 MeV, 6.39 MeV, and 5.09 MeV, are all easily seen. The 7.64-MeV and 7.13-MeV lines are from the iron in the capsule and in the sand. The 4.95-MeV energy line indicates carbon. This striking background capture γ-spectrum could interfere with many of the prompt γ-peaks of elements of interest on the ocean floor. However, the energy lines of chlorine proved useful for detector calibration.

Marine manganese nodules in an ocean environment

Marine manganese nodules are quite closely located in fields on the ocean floor. To simulate such a field, six nodules from the Blake Plateau, a total weight of *ca.* 3 pounds, were lowered onto the sand near the source (Fig. 9). Figure 10 shows the resultant capture γ-spectrum after a 40-min run. The chlorine peaks are clearly evident. However, manganese can be identified from the presence of the small full peaks at 7.06 MeV and 5.92 MeV, as well as from the single escape peaks at 6.55 MeV and 5.25 MeV, and the double escape peaks at 6.22 MeV, 6.04 MeV and 5.76 MeV. The spectral signature of a trio of peaks seen three times for pure manganese is altered by other elements. The full peak at 7.16 MeV is masked by the 7.13-MeV peak of iron and the 7.24-MeV peak is blocked by the 7.28-MeV peak of chlorine, but the 7.06 MeV peak is visible. The single escape peak of manganese at 6.55 MeV is seen but the 6.65 MeV peak is masked by both the 6.62-MeV Fe (d) and the 6.62-MeV Cl (d) peaks.

Nevertheless, the double escape peaks of manganese at 6.04 MeV and 6.22 MeV are unaltered. The 6.14-MeV peak is masked by the 6.11-MeV peak of chlorine.

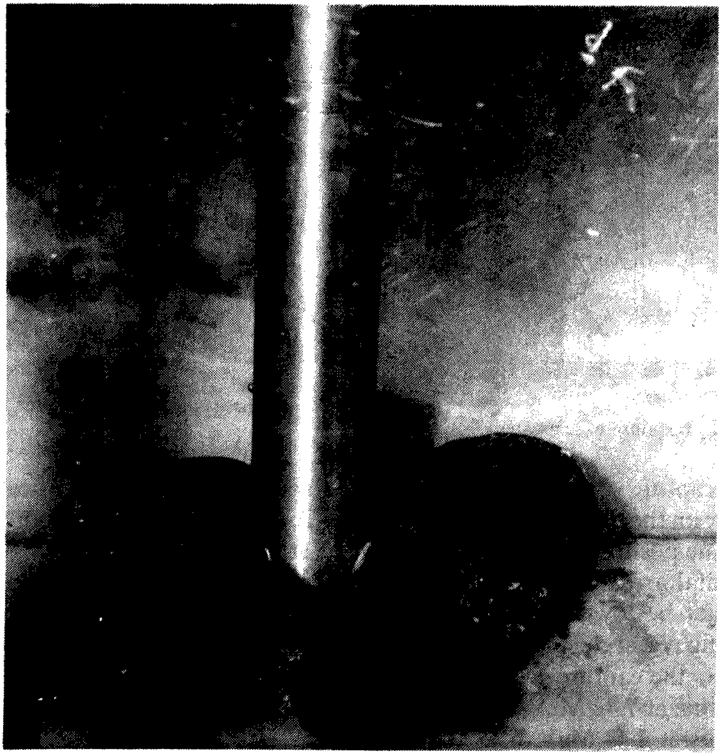


Fig. 9. Simulated marine environment—manganese nodules near ^{252}Cf source.

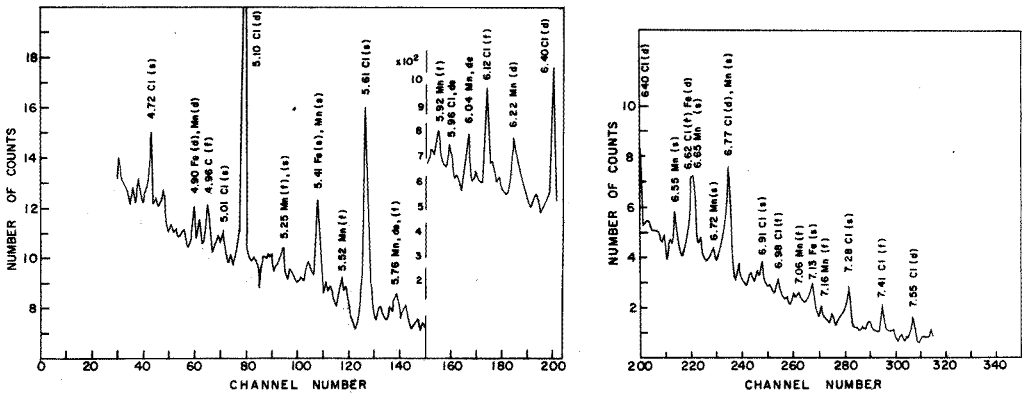


Fig. 10. Neutron capture γ-ray spectrum of manganese nodules on silica sand in sea water.

Other peaks such as the 5.41 MeV and 4.90 MeV can be mainly attributed to the iron in the nodule.

Although this complicated spectrum requires detailed study, manganese peaks can be seen at the energy lines predicted by both reactor and ^{252}Cf irradiations of pure manganese dioxide and manganese nodules in the presence of salt water and sand.

CONCLUSIONS

This work shows that neutron capture γ-rays can be used for element identification in marine manganese nodules. An *in situ* system consisting of a neutron source, *e.g.*, submarine, accelerator, or isotopic source, and a Ge(Li) detector would appear to be useful in locating valuable materials such as manganese on the ocean floor, as well as allowing general surveys of the composition of marine sediments and rocks. Based on present experience, the compactness and portability of the californium source make it attractive for *in situ* applications.

The authors are indebted to the Savannah River Operations Office of the U.S. Atomic Energy Commission and to Dr. N. Stetson for making the ^{252}Cf source available, and to Dr. Frank E. Senftle of the U.S. Geological Survey for the use of laboratory facilities.

SUMMARY

The analysis of manganese nodules formed on the ocean floor is of current interest. Neutrons from the thermal column of a 10-kW pool-type research reactor and a 120-μg californium-252 source were used to study the prompt photon emissions from neutron capture in these nodules. Despite the complex spectra obtained by irradiation of sea water, it is possible to detect and estimate manganese in nodules by means of the peaks at 7.06, 6.55, 6.22 and 6.04 MeV. A possible *in situ* experimental arrangement is discussed.

RÉSUMÉ

L'analyse de nodules de manganèse, formés au fond des océans, présente un intérêt tout particulier. Des études sont effectuées à l'aide de rayons gamma, à capture neutronique, en utilisant un réacteur nucléaire de recherche et une source de californium-252. Malgré les spectres complexes obtenus par irradiation de l'eau de mer, il est possible de déceler et de doser le manganèse dans des nodules, au moyen des pics de 7.06, 6.55, 6.22 et 6.04 MeV.

ZUSAMMENFASSUNG

Die Analyse von Mangan-Knollen, die sich auf dem Meeresgrund gebildet haben, ist von allgemeinen Interesse. Neutronen aus dem thermischen Rohr eines 10 kW-Forschungsreaktors vom Pool-Typ und eine 120-μg Californium-252-Quelle wurden verwendet, um die prompten Photonenemissionen in diesen Knollen nach Neutroneneinfang zu untersuchen. Trotz der komplexen Spektren, die bei Bestrahlung von Meerwasser erhalten werden, ist est möglich, Mangan in den Knollen mit Hilfe der Peaks bei 7.06, 6.55, 6.22 und 6.04 MeV nachzuweisen und zu bestimmen. Eine mögliche experimentelle Anordnung für *in situ*-Untersuchungen wird diskutiert.

REFERENCES

1 Ocean Bottom Minerals, *Ocean Ind.*, Vol. 3, No. 6 (1968).
2 Staff Report, *Undersea Technol.*, Vol. 10, No. 1 (1969).

3 N. C. Rasmussen, Y. Hukai, T. Inouye and V. Orphan, *Report No. MIT NE*-85, 1969.
4 R. C. Greenwood and J. H. Reed, *Report No. IITRI*—1193-53, 1965.
5 L. V. Groshev, A. M. Dividov, V. N. Lutsenko and V. I. Pelekov, *J. Nucl. Energy*, 8 (1958) 127.
6 G. A. Bartholomew and B. B. Kinsey, *Phys. Rev.*, 89 (1953) 386.
7 A. A. El Kady, Ph. D. Thesis, University of Maryland, 1969.
8 J. Hays, Lamont-Doherty Geological Observatory of Columbia University, private communication.
9 H. W. Menard, *Marine Geology of the Pacific*, McGraw-Hill, New York, 1964, p. 174.
10 J. A. Smith, *Californium*-252 *U.S.A.E.C. Report Con. F.* 681032, 1969.
11 W. C. Reinig and A. G. Evans, *The* 1968 *Int. Conf. on Mod. Trends in Act. Anal.*, U.S.N.B.S. No. 33, 1968, p. 116.
12 P. F. Wiggins and D. Hickey, *Nav. Eng. J.*, 81, No. 5 (1969) 79.

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NON-FLAME ATOMIC ABSORPTION IN THE VACUUM ULTRAVIOLET REGION

THE DIRECT DETERMINATION OF MERCURY IN AIR AT THE 184.9-nm RESONANCE LINE

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Current environmental concern over the dangers of mercury pollution has prompted a great increase in the number of publications on the determination of mercury in the analytical literature. This has been especially so in the field of atomic spectroscopy where non-flame atom cells have been successfully employed for both atomic absorption and atomic fluorescence determinations of mercury. All of these published results have utilized the spin-forbidden resonance line at 253.7 nm, caused by the transition 6^1S_0–6^3P_1. While it has long been known that the resonance line at 184.9 nm (6^1S_0–6^1P_1) has an oscillator strength some fifty times greater than this[1], the analytical potential of this line has not been exploited to date. That is has not been, is due in part to the difficulty of working in the vacuum ultraviolet and also to the fact that the flame atomizers used are not sufficiently transparent in this region. However, since the advent of non-flame atomizers, the latter objection is no longer valid.

Based on the oscillator strength of the 184.9-nm mercury line an increase in sensitivity of at least an order of magnitude compared to the 253.7-nm absorption line would be predicted.

Previously, systems for the continuous direct measurement of lead[2], and cadmium and mercury[3] in air have been described. In the work reported here, the Hg 184.9-nm resonance line has been successfully exploited to increase the sensitivity of the measurement over the 253.7-nm line by greater than an order of magnitude. The range of atomic-absorption measurements is thus extended into the vacuum ultraviolet down to 184.9 nm.

Several mercury light sources which are used routinely in atomic absorption work have been investigated with regard to the relative sensitivities of the 184.9 and 253.7-nm lines. It was found that the sensitivity varied greatly from lamp to lamp, probably because of self-absorption.

EXPERIMENTAL

The equipment used is listed in Table I.

The non-flame cell utilized spectrographically pure carbon rods 10–20 mm in length heated with a Lepel 5000-W radiofrequency generator and a 10-turn 120-

TABLE I

EXPERIMENTAL APPARATUS

Monochromator: Jarrell-Ash 82-500, 0.5 m with 100-μm fixed slits, modified to allow purging.
Radiation sources: 1. Hg pen lamp (Ultraviolet Products)
2. General Electric OZ 4511 ozone lamp
3. Perkin-Elmer Hg hollow cathode
4. Glomax demountable hollow-cathode lamp (Barnes Engineering Company) with GPS-1 HCL power supply and gas control unit.
Hydrogen lamp: Beckman Instruments
Detector: Jarrell-Ash R106 photomultiplier.
Detector power supply: Hewlett-Packard Harrison 6515-A d.c. power supply.
Amplifier: P.A.R. Model 126 lock-in amplifier with Model 184 photometric preamplifier.
Recorder: Beckman Model 10005 10-in. potentiometric strip-chart recorder.
Air pump: Bantam Model 7064 pressure and suction laboratory pump.
External optics: Two quartz 30-mm diameter plano-convex lenses—100-mm focal length.
Mechanical chopper: Jarrell-Ash chopper assembly driven at 87 Hz, modified with photocell to supply reference signal to amplifier.
Motor-driven syringe: SAGE Instruments, Inc., Model 234-1.

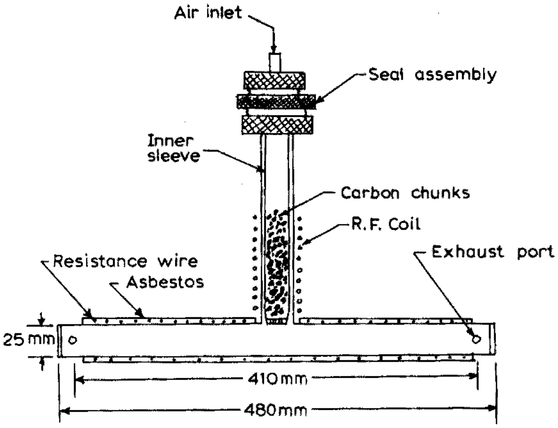


Fig. 1. The quartz absorption tube.

mm copper coil. The temperature of the rods, determined by means of an optical pyrometer, was *ca.* 1350°. The quartz absorption tube was heated to *ca.* 900° by 700-W nichrome resistance heaters. A diagram of the absorption tube is shown in Fig. 1, and a schematic diagram of the entire measurement system is shown in Fig. 2. As air was drawn through the bed of hot carbon the oxygen was converted to carbon monoxide and metallic compounds in the air were reduced to the atomic state either by reaction with hot carbon or carbon monoxide.

Sensitivity measurements and calibration

Clean air. Cold activated charcoal was shown to be an efficient scrubbing agent for removing mercury from the air. Results showed that air taken directly from cylinders of compressed air gave the same signal even after passing through an

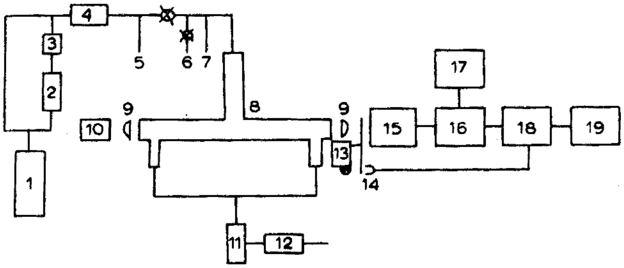


Fig. 2. Schematic diagram of measurement system.
(1) Compressed air tanks.
(2) Activated charcoal filter.
(3) Millipore filter.
(4) Flow meter.
(5) Bleed off vent.
(6) Ambient air inlet.
(7) Injection inlet.
(8) Quartz tube.
(9) Plano-convex lenses.
(10) Light source.
(11) Flow meter.
(12) Diaphragm pump.
(13) Chopper.
(14) Reference signal.
(15) Monochromator.
(16) Photomultiplier.
(17) Photomultiplier power supply.
(18) Lock-in amplifier
(19) Recorder.

activated charcoal bed and millipore filter (Fig. 2). Compressed air was taken as "clean air" for these studies.

Calibration. Air saturated with mercury vapor at a known temperature was injected into clean air flowing into the system. The saturated air was injected by a motor-driven syringe.

The air flow rate was 1.0 l min^{-1}. The concentration of mercury injected was calculated from vapor pressure data[4]. For example, at 20° if the saturated vapor was injected at 1 ml min^{-1} this was equivalent to 13.3 ng l^{-1} min^{-1} or 13.3 μg m^{-3}. By varying the injection rate, the final mercury concentration introduced into the air was varied.

The results are summarized in Fig. 3. The improved sensitivity obtained at the 184.9-nm line can be seen.

Sensitivity. The sensitivity limit defined as that signal to give 1% absorption was 0.1 μg m^{-3}. The detection limit defined as that signal equivalent to 0.66 noise level was 0.5 μg m^{-3}. This could be improved by the use of damping equipment.

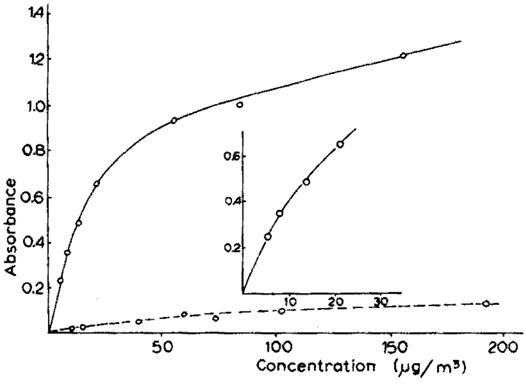


Fig. 3. Calibration curves obtained with the fused $HgCl_2$ cathode in the Barnes Demountable HCDT at 184.9 nm (—) and 253.7 nm (---).

Mercury lamp source evaluation

Normal operating conditions. The atomizer used operated at a lower temperature than flames. The Doppler effect and Lorentz broadening were therefore less. Consequently the absorption lines would be narrower. Any self-absorption by the source of its own resonance lines would be more critical because self-absorption takes place at the very center of the resonance lines.

With mercury, the absorption is further complicated by the fact that the metal exists in seven stable isotopes, each of which is capable of absorbing the wings of the emission lines of other isotopes. Consequently, even with complete self-absorption by the source, some absorption by the sample would always be observed.

Various mercury lamp sources were investigated. The studies were carried out under normal operating conditions. The results are shown in Fig. 4.

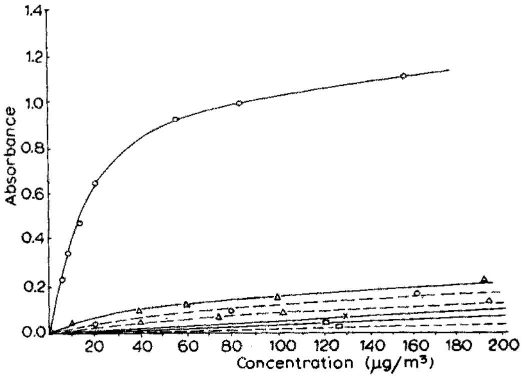


Fig. 4. Analytical curves obtained with different mercury sources under normal operating conditions. (—) 184.9 nm; (---) 253.7 nm; (○) Fused salt DHCL; (△) amalgam DHCL; (×) OZ lamp; (□) pen lamp.

Measured amounts of saturated mercury vapor at known temperatures were injected into an air stream through a rubber septum (Fig. 2)[5]. In this way a known weight of mercury was injected into the air stream, and the absorption was measured. The volume of the absorption tube was *ca.* 200 ml. With no pretence of rigor or exact accuracy, since only comparative measurements were of interest, an estimate of the concentration corresponding to a given absorbance was obtained by assuming that the peak absorbance values occurred when all of the injected mercury vapor was distributed throughout the light path of the absorption tube. This estimate seemed reasonable in view of the fact that from the first occurrence of the signal to the peak value took 0.2 min. A more accurate calibration procedure with a continuous injection system showed it to be $< 20\%$ relative error. It was felt that the precision was sufficiently high to enable a comparative evaluation.

The shapes of the analytical curves obtained with four different mercury sources at both 184.9 and 253.7 nm are as shown in Fig. 4. (It was not possible to observe the 184.9-nm line in the case of the sealed commercial hollow-cathode lamp.) It appeared that the Barnes demountable hollow-cathode lamp was the most sensitive source.

Two types of hollow cathodes were used in the demountable lamp. In one case, a solid copper hollow cathode was amalgamated with elemental mercury;

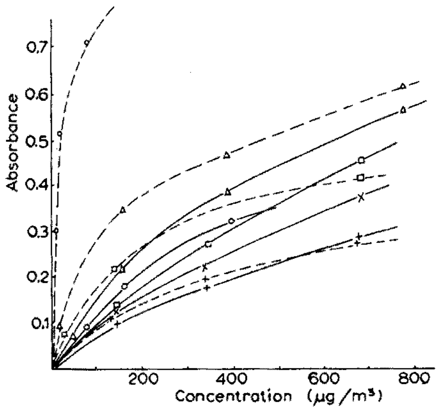
in the second case the cathode was filled with mercury(II) chloride and fused at 280°. The use of the fused salt was found to be more sensitive at 184.9 nm than any of the sources studied, especially at the concentrations of interest in this work. (The M.A.K. value for mercury in air is 100 µg m^{-3} [6].)

It is of interest to note that for both the pen lamp and G.E. OZ lamp there was no pronounced gain in sensitivity in using the 184.9-nm line rather than the 253.7-nm resonance line. This may be explained by the absorption by mercury isotopes of the wings of resonance lines of other mercury isotopes. This isotope effect may also explain the flattening of the calibration curves at low absorption levels. It was felt that all available radiation at the center of the resonance lines had been self-absorbed at this point and only unabsorbable light was reaching the detector. When the demountable hollow-cathode lamp was employed, especially with the fused mercury(II) chloride cathode, less free mercury was available in the lamp to cause self-reversal and an increase in sensitivity was obtained. This source was used to monitor the ambient air.

Room temperature studies

For completeness the studies were also carried out with the absorption tube at room temperature with inherently narrower mercury absorption lines. The radiofrequency inductor was not used and carbon was not placed in the absorption tube. Nitrogen was used as the flow gas in order to observe the 184.9-nm line. These results may be of interest to users of mercury analyzers or workers involved in the determination of mercury by a cold vapor technique. They are shown in Fig. 5.

The effect of temperature on the degree of absorption. A comparison of Figs. 4, 5 and 6 shows that equal amounts of mercury absorbed more strongly at room temperatures than at the operating temperature of the absorption tube (900°).



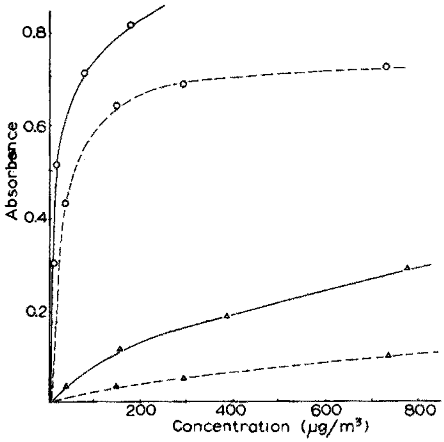


Fig. 5. Analytical curves obtained with different mercury sources under cold vapor conditions. (—) 253.7 nm; (---) 184.9 nm. (○) Fused salt DHCL; (△) amalgam DHCL. (□) OZ lamp; (×) Sealed hollow cathode; (+) pen lamp.

Fig. 6. Analytical curves obtained at 184.9 nm under "hot" (900°) and "cold" (20°) vapor conditions. (---) Hot; (—) Cold. (○) Demountable HCL; (△) pen lamp.

At first glance these results are perplexing. At higher temperatures broadening of the absorption line would be expected, resulting in a greater overlap between absorption line and the center of the emitted line from the source. An increase in absorption would be expected to result from this broadening.

The other factors affecting total absorption include N, the number of atoms in the light path, and f, the oscillator strength.

Increasing the temperature from room temperature (20°) to 900° would decrease the population at ground state and increase the population in the excited state if the total population is constant. However, the transition requires a lot of energy ($E = h\nu$, $\nu = c/\lambda$, $\lambda = 184.9$ or 253.7 nm) and this redistribution of atoms to the excited state must be vanishingly small.

It should also be noted that increasing the temperature will increase the volume of a given quantity of air. N'_1, the number of atoms in a constant volume, would therefore decrease at increased temperature. However, it is believed that N, the total number of atoms in the light path, is not diminished when the sample injection system described is used.

The third factor is the oscillator strength. Two equations mathematically defining the oscillator strength are[4]:

$$f_{21} = \frac{mc}{8\pi^2 e^2} \frac{g_1}{g_2} \lambda_{21}^2 A_2^1 \qquad (1)$$

and

$$f_{21} = \frac{\tau_0}{3\tau_2} \frac{g_2}{g_1} \qquad (2)$$

Considering the components of these equations, the first reaction would be that a decrease in absorption with increased temperature would not be expected.

This phenomenon is being studied further.

STUDIES ON THE DIRECT DETERMINATION OF MERCURY IN THE ATMOSPHERE AT 184.9 NM

Molecular absorption

One of the greatest difficulties in atomic absorption in the vacuum ultraviolet is the high level of molecular absorption. A great many inorganic and organic species show wide-band molecular absorption below 200.0 nm. These have been well documented by Kaye[5,7].

In the system described in Fig. 1 it was expected that the useful range could be extended to 185.0 nm. To this end, the air in the monochromator was replaced by argon, thus removing the highly absorbing oxygen, and the nitrogen which absorbs increasingly as the wavelength decreases.

The atmosphere in the sample light path was nitrogen plus carbon monoxide formed during the reduction stage. It was felt that absorption by these compounds would not be insignificant, neither would it be excessive.

In practice it was found that the introduction of ambient air into the system resulted in a higher molecular absorption than when clean air was introduced. Any variable molecular absorption must be corrected for or eliminated in order to avoid error. It was found that the molecular absorption of ambient air showed the same broad band structure as that of clean air with water vapor added. Under the experimental conditions, any water vapor was reduced according to the water gas reaction $C+H_2O \rightarrow CO+H_2$, and it was found that hydrogen absorbed over this wavelength range. Variation in humidity of atmospheric samples would lead to variable molecular absorption. No attempt was made to characterize any other absorbing species. The degree of molecular absorption was found to vary from day to day and corrections to overcome this were therefore necessary. Elimination of the interference by drying agents introduced the possibility of scrubbing both particulate and non-particulate matter of interest out of the air and would lead to low analytical results.

Correction for molecular absorption

Correction was achieved by setting the monochromator on the 184.9-nm resonance line and using a hydrogen lamp as the light source. With 100-μm slits the band pass of the monochromator was 0.125 nm, and so the absorption observed in this case was primarily molecular.

In order to determine the lowest level of molecular absorption, a study was made on the effect of flow rate on the molecular absorption of ambient air. As shown in Fig. 7, a minimum occurred around 1.0 l min^{-1} and this flow rate was used. The atomic absorption signal from ambient air was easily measurable at flow rates of 1.0 l min^{-1}.

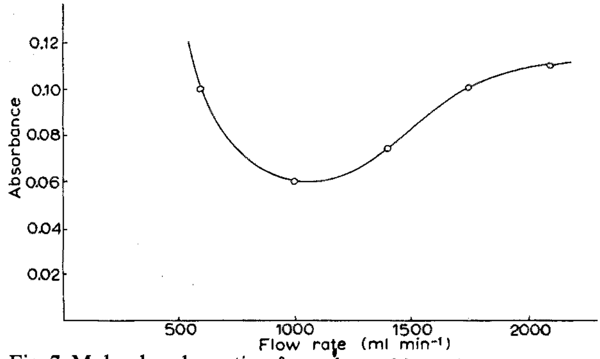


Fig. 7. Molecular absorption from the ambient air at 184.9 nm as a function of flow rate.

Procedure for continuous determination of mercury in air

In order to determine the mercury content of the ambient air the following procedure was followed. With the line source at 184.9 nm, the signal was adjusted to the 100% line with clean air flowing through the system. The clean air supply was then cut off and the ambient air drawn through the system. The measured signal is due to both molecular and atomic absorption. If necessary, this was repeated until a reliable mean was obtained. The line source was then replaced by the hydrogen lamp and the process repeated. The measured signal in this case is due to molecular absorption (the contribution of atomic absorption being negligible). Subtraction of the two mean values yielded the signal from atomic absorption. From the calibration curve for that day the concentration could then be deduced. Laboratory air samples

TABLE II

RESULTS OF MERCURY DETERMINATIONS OF LABORATORY AIR IN BATON ROUGE, LA.

Date	*Mercury concentration* ($\mu g\ m^{-3}$)
3-3-72	14
3-6-72	30
3-7-72	8
3-8-72	15
3-9-72	10
3-13-72	5
3-14-72	1

were drawn into the instrument over a period of weeks; the results are listed in Table II.

Detection of arsenic and selenium

A preliminary study was made on the feasibility of the determination of arsenic and selenium in the ambient atmosphere. With commercially available hollow-cathode lamps, the resonance lines at 193.7 and 196.0 nm were strong and stable in the system. Ambient air signals monitored gave large absorption values. However, indications were that the greater part of these signals was due to molecular absorption with a small atomic contribution. Investigations are in progress to calibrate the system for both arsenic and selenium and determine the obtainable sensitivities and detection limits.

CONCLUSIONS

The system described extends atomic absorption measurements into the vacuum ultraviolet down to 184.9 nm. Molecular absorption can be simply corrected for and the path is open to resonance lines below 200.0 nm. These include the lines for arsenic and selenium,which are both of great interest in environmental studies. The use of the mercury resonance line at 184.9 nm is the first reported use of this line in analytical atomic absorption to our knowledge, and, as has been shown, represents a great increase in sensitivity over the line routinely used in atomic absorption work. This system can also be used to record atomic absorption signals of arsenic and selenium in the ambient air. The determination of these elements will form the basis of a future article.

This investigation was supported by Research Grant AP 0086-03, Air Pollution Control Office, Environmental Protection Agency.

SUMMARY

Mercury in the atmosphere was analyzed continuously without prior scrubbing or sample collection. The mercury resonance line at 184.9 nm was utilized. This was made possible with an r.f. carbon rod atomizer and by pumping the monochromator with argon; the sensitivity was 0.1 μg Hg m^{-3}. The method was sensitive to the type of mercury light source used. Strong reversal of the resonance lines on commercial hollow cathodes was indicated. Some anomalous temperature affects were observed.

RÉSUMÉ

On propose une méthode d'analyse du mercure dans l'atmosphère sans épuration préalable et prise d'échantillon. On procède par absorption atomique sans flamme, en utilisant la raie de résonance à 184.9 nm. La sensibilité est de 0.1 μg Hg m^{-3}.

ZUSAMMENFASSUNG

Quecksilber in der Atmosphäre wurde kontinuierlich ohne vorheriges Konzentrieren oder Probensammeln analysiert. Es wurde die Quecksilber-Resonanzlinie bei 184.9 nm verwendet. Dies wurde durch einen Graphitstab-Atomisator und durch Spülung des Monochromators mit Argon ermöglicht; die Empfindlichkeit war 0.1 μg Hg m^{-3}. Die Methode wurde durch die Art der Quecksilber-Lichtquelle beeinflusst. Bei handelsüblichen Hohlkathodenlampen wurde eine starke Umkehr der Resonanzlinien festgestellt. Einige anomale Temperatureinflüsse wurden beobachtet.

REFERENCES

1 A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms*, Cambridge University Press, 1961.
2 H. P. Loftin, C. M. Christian and J. W. Robinson, *Spectrosc. Lett.*, 3 (1970) 161.
3 C. M. Christian and J. W. Robinson, *Anal. Chim. Acta*, 56 (1971) 466.
4 H. S. Taylor and S. Glasstone, *A Treatise on Physical Chemistry*, Vol. I, D. Van Nostrand, 3rd Ed., 1942, p. 356.
5 W. I. Kaye, *Appl. Spectrosc.*, 15 (1961) 130.
6 W. Leithe, *The Analysis of Air Pollutants*, Ann Arbor-Humphrey Science Publishers, 1970.
7 W. I. Kaye, *Appl. Spectrosc.*, 15 (1961) 89.

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THE EFFECT OF LOW CONCENTRATIONS OF MISCIBLE ORGANIC SOLVENTS ON THE DETERMINATION OF TRACE METALS IN WATER SAMPLES BY ATOMIC ABSORPTION SPECTROMETRY

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Since the use of organic solvents was introduced into flame spectrophotometry by Dean and Lady[1], numerous applications have been described. In the field of atomic absorption spectrometry, most applications of organic solvents have been for the purpose of signal enhancement. Many explanations have been proposed to explain the enhancement effects which are observed in the presence of organic solvents. Lockyer *et al.*[2] describe the enhancement as a result of changes in the transient conditions that exist as the solvent evaporates in the flame. Allan[3] concludes that the increased sensitivity results from an increase in the amount of solution reaching the flame. Belcher *et al.*[4] reported solvent enhancement to be caused principally by an increase of atomization relative to aqueous solutions. Winefordner *et al.*[5] attribute the increase in absorption primarily to the increase in sample introduction efficiency. Robinson[6] lists several possible causes of signal enhancement including the change in sample feed rate with solvents of different viscosities, the effect of surface tension on drop size, and the effect of increased efficiency of producing neutral atoms in the flame. Chakrabarti and Singhal[7] describe the enhanced signal as being due to such factors as production of smaller droplets, smaller and more volatile clotlets lower in the flame and thermal dissociation and chemical reduction of the metal oxide.

It is extremely difficult experimentally to isolate and study individually the effect of a single factor in the enhancement of sensitivity. All of the above factors are probably present, but certain factors may be predominant in some cases and less predominant in other cases. Regardless of the mechanism involved, it is well established that organic solvents do have an enhancing effect on atomic absorption signals.

Application of organic solvents in atomic absorption has been primarily for the purpose of absorption enhancement. To obtain significant absorption enhancement, solvent concentrations from 25 to 100% have been normally recommended. The work described in this report was undertaken to determine the effect, if any, of low concentrations of miscible organic solvents on the determination of trace quantities of metals in wastewater streams. As a result of the U.S. Army Corps of Engineers Permit System, the determination of trace metals in wide variety of wastewater streams has taken on a special emphasis. Many waste streams contain small amounts of organic solvents which could have an enhancing effect, thus causing a high result. The numerous literature references to the use of organic solvents in atomic absorption have been primarily interested in only the enhancement effect, and little or no data are available on the effects of low concentrations of organic solvents. Therefore, this investigation was undertaken to determine the effects of low concentrations of organic solvents on atomic absorption determinations.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 303 atomic absorption spectrophotometer equipped with a standard Perkin-Elmer premix burner using air and acetylene was employed for all determinations. Standard operating parameters[8,9] are shown in Table I.

TABLE I

OPERATING PARAMETERS[a]

Metal	*Wavelength (nm)*	*Current (mA)*	*Fuel flow (cm^3 min^{-1})*
Co	240.72	30	2600
Cr	357.87	30	3300
Cu	324.75	30	2600
Fe	248.33	30	2600
Cd	228.80	10	2600
Be	234.86	30	2600
Na	588.99	900	2600
Ca	422.67	30	2600

[a] In all cases a slit width of 4 nm was used and the oxidizer flow (SCFH) was 27.5.

Reagents

Ethanol (USI) 200 proof, acetic acid, ethyl acetate and acetone (Eastman Organic Chemicals) were used without further purification. Stock solutions containing 1% metal (Aztec Instruments Inc.) were used to prepare all metal solutions required.

Procedure

Standard aqueous solutions containing cobalt, chromium, copper, iron, cadmium and calcium in concentrations of 1, 3 and 5 p.p.m. were prepared. Solutions containing 3 p.p.m. of each of the metals were prepared and diluted to contain 0.05, 0.1, 0.5, 1.0 and 5.0% of the following organic solvents: ethanol, acetone, ethyl acetate and acetic acid. The concentrations of the 3 p.p.m. metal solutions were determined by atomic absorption with the operating parameters given in Table I. The 1 and 5 p.p.m. solutions were used as standards, and the apparent concentrations of the 3 p.p.m. samples were determined by use of the following equation:

$$\text{apparent concentration} = \left[(A-A_1)\left(\frac{C_2-C_1}{A_2-A_1}\right)\right] + C_1$$

where A = the absorbance of the sample; A_1 = the absorbance of the less concentrated standard; A_2 = the absorbance of the more concentrated standard; C_1 = the concentration of the less concentrated standard; C_2 = the concentration of the more concentrated standard.

TABLE II

EFFECT OF ACETIC ACID

Solvent added (%)	0	0	0	0.05	0.1	0.5	1.0	5.0
Concn. (*p.p.m.*)	1	5	3	3	3	3	3	3
Cobalt								
Absorbance	0.0287	0.1296	0.0799	0.0799	0.0794	0.0799	0.0814	0.0851
Concn. found	—	—	3.03	3.03	3.01	3.03	3.09	3.24
% Rel. error			0	0	0	0	2.0	6.9
Chromium								
Absorbance	0.0400	0.1726	0.1085	0.1085	0.1085	0.1090	0.1113	0.1141
Concn. found	—	—	3.07	3.07	3.07	3.08	3.15	3.24
% Rel. error			0	0	0	0.33	2.6	4.6
Copper								
Absorbance	0.0462	0.2211	0.1349	0.1349	0.1343	0.1355	0.1367	0.1439
Concn. found	—	—	3.03	3.03	3.01	3.04	3.07	3.23
% Rel. error			0	0	0	0.33	2.0	6.6
Iron								
Absorbance	0.0177	0.1079	0.0645	0.0645	0.0645	0.0645	0.0660	0.0721
Concn. found	—	—	3.08	3.08	3.08	3.08	3.14	3.41
% Rel. error			0	0	0	0	2.0	10.7
Cadmium								
Absorbance	0.0888	0.3665	0.2411	0.2403	0.2396	0.2403	0.2434	0.2549
Concn. found	—	—	3.19	3.18	3.17	3.18	3.23	3.39
% Rel. error			0	0	0	0	1.6	6.6
Beryllium								
Absorbance	0.0186	0.0947	0.0565	0.0565	0.0570	0.0590	0.0605	0.0660
Concn. found	—	—	0.299	0.299	0.302	0.312	0.320	0.349
% Rel. error			0	0	1.0	4.3	7.0	16.7
Sodium								
Absorbance	0.0287	0.1314	0.0788	0.0778	0.0778	0.0814	0.0773	0.0820
Concn. found	—	—	0.295	0.291	0.291	0.305	0.289	0.308
% Rel. error			0	0	0	4.8	—	5.8
Calcium								
Absorbance	0.0521	0.2373	0.1487	0.1487	0.1487	0.1506	0.1555	0.1643
Concn. found	—	—	3.09	3.09	3.09	3.13	3.23	3.42
% Rel. error			0	0	0	1.3	4.5	10.7
Aspiration ($cm^3 min^{-1}$)	3.6	3.6	3.6	3.6	3.5	3.5	3.5	3.4

Beryllium and sodium were evaluated in the same manner but at concentrations of 0.1, 0.3 and 0.5 p.p.m.

The aspiration rate was determined for each sample and is recorded in Tables II through V.

RESULTS AND DISCUSSION

The purpose of this investigation was to determine the effects, if any, of small amounts of miscible organic solvents on the atomic absorption of various metals. Since wastewater streams may contain a wide variety of organic solvents, enhancements caused by their presence may be an important factor. Cobalt, chromium, copper, iron, beryllium, sodium and calcium were chosen because of the interest

TABLE III

EFFECT OF ETHYL ACETATE

Solvent added (%)	0	0	0	0.05	0.1	0.5	1.0	5.0
Concn. (*p.p.m.*)	1	5	3	3	3	3	3	3
Cobalt								
Absorbance	0.0250	0.1152	0.0706	0.0706	0.0711	0.0737	0.0757	0.0814
Concn. found	—	—	3.02	3.02	3.04	3.16	3.25	3.50
% Rel. error			0	0	0.7	4.6	7.6	15.9
Chromium								
Absorbance	0.0339	0.1463	0.0910	0.0910	0.0910	0.0942	0.0943	0.1018
Concn. found	—	—	3.03	3.03	3.03	3.15	3.15	3.42
% Rel. error			0	0	0	4.0	4.0	12.9
Copper								
Absorbance	0.0443	0.2076	0.1249	0.1255	0.1261	0.1290	0.1308	0.1469
Concn. found	—	—	2.97	2.99	3.00	3.07	3.12	3.51
% Rel. error			0	0	0	2.7	4.3	17.3
Iron								
Absorbance	0.0246	0.1273	0.0768	0.0768	0.0768	0.0783	0.0788	0.0888
Concn. found	—	—	3.03	3.03	3.03	3.09	3.11	3.50
% Rel. error			0	0	0	2.0	2.6	15.5
Cadmium								
Absorbance	0.0778	0.3401	0.2175	0.2175	0.2175	0.2211	0.2262	0.2426
Concn. found	—	—	3.13	3.13	3.13	3.19	3.26	3.51
% Rel. error			0	0	0	1.9	4.2	12.1
Beryllium								
Absorbance	0.0278	0.1090	0.0625	0.0625	0.0625	0.0650	0.0680	0.0814
Concn. found	—	—	0.271	0.271	0.271	0.283	0.298	0.364
% Rel. error			0	0	0	4.4	10.0	34.3
Sodium								
Absorbance	0.0410	0.1273	0.0799	0.0783	0.0762	0.0799	0.0878	0.0915
Concn. found	—	—	0.280	0.273	0.263	0.280	0.317	0.334
% Rel. error			0	0	0	2.5	16.1	18.2
Calcium								
Absorbance	0.0590	0.2573	0.1599	0.1612	0.1612	0.1637	0.1681	0.1858
Concn. found	—	—	3.04	3.06	3.06	3.11	3.20	3.56
% Rel. error			0	0	0	2.3	5.3	17.1
Aspiration (cm^3 min^{-1})	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.3

in the determination of these elements in wastewater samples. The four solvent systems evaluated were chosen to represent four different chemical classes of miscible organic solvents that might be found in various wastewater streams.

Tables II through V show the data obtained in these experiments. In all cases the sample containing the organic solvent was analyzed by comparison with a standard of higher and lower concentrations prepared in distilled water. The data obtained indicate that little or no enhancement is observed at organic solvent concentrations of 0.1% or less. This observation appears to be valid regardless of the metal or solvent system involved. At higher organic solvent concentrations, *i.e.*, 0.5–1.0%, an enhancement from 2 to 16% relative is not uncommon. Both the metal and solvent systems affect the magnitude of the absorption enhancement. General statements

TABLE IV

EFFECT OF ETHANOL

Solvent added (%) *Concn.* (*p.p.m.*)	0 1	0 5	0 3	0.05 3	0.1 3	0.5 3	1.0 3	5.0 3
Cobalt								
Absorbance	0.0218	0.1002	0.0615	0.0615	0.0615	0.0620	0.0615	0.0650
Concn. found	—	—	3.03	3.03	3.03	3.05	3.03	3.20
% Rel. error			0	0	0	0.66	0	5.6
Chromium								
Absorbance	0.0386	0.1746	0.1107	0.1107	0.1107	0.1113	0.1129	0.1232
Concn. found	—	—	3.12	3.12	3.12	3.14	3.19	3.49
% Rel. error			0	0	0	0.64	2.2	11.9
Copper								
Absorbance	0.0472	0.2328	0.1421	0.1409	0.1409	0.1421	0.1475	0.1561
Concn. found	—	—	3.05	3.02	3.02	3.05	3.16	3.35
% Rel. error			0	0	0	1.0	4.6	10.9
Iron								
Absorbance	0.0241	0.1244	0.0762	0.0762	0.0778	0.0783	0.0783	0.0846
Concn. found	—	—	3.08	3.08	3.14	3.16	3.16	3.41
% Rel. error			0	0	1.9	2.6	2.6	10.7
Cadmium								
Absorbance	0.0680	0.2823	0.1858	0.1858	0.1858	0.1898	0.1918	0.2020
Concn. found	—	—	3.20	3.20	3.20	3.27	3.31	3.50
% Rel. error			0	0	0	2.2	3.4	9.4
Beryllium								
Absorbance	0.0155	0.0883	0.0511	0.0511	0.0511	0.0511	0.0511	0.0595
Concn. found	—	—	0.296	0.296	0.296	0.296	0.296	0.342
% Rel. error			0	0	0	0	0	15.5
Sodium								
Absorbance	0.0353	0.1308	0.0783	0.0794	0.0783	0.0783	0.0794	0.1029
Concn. found	—	—	0.280	0.285	0.280	0.280	0.285	0.383
% Rel. error			0	1.8	0	0	1.8	36.8
Calcium								
Absorbance	0.0506	0.2255	0.1439	0.1433	0.1433	0.1465	0.1512	0.1656
Concn. found	—	—	3.13	3.12	3.12	3.19	3.30	3.63
% Rel. error			0	0	0	2.2	5.8	16.3
Aspiration ($cm^3 min^{-1}$)	3.7	3.7	3.7	3.7	3.7	3.7	3.7	3.3

concerning enhancement effects at higher solvent concentrations are therefore not reliable and each case must be considered individually.

When observing the effect of ethyl acetate at the 1% level, it is obvious that some metals are enhanced more than are others. For example, sodium and beryllium are enhanced by more than 10% while the enhancement for cobalt is *ca.* 7%; and for all other metals, the enhancement is less than 5%. The effect of different solvents also can be observed. At the 1% solvent level, beryllium has an enhancement of 10, 7 and 0% in ethyl acetate, acetic acid and acetone, respectively. These same relationships can be observed with various combinations of metal and solvent. At the 5% solvent concentration, all elements and solvent systems indicate significant absorption enhancement.

TABLE V

EFFECT OF ACETONE

Solvent added (%)	0	0	0	0.05	0.1	0.5	1.0	5.0
Concn (*p.p.m.*)	1	5	3	3	3	3	3	3
Cobalt								
Absorbance	0.0223	0.1035	0.0650	0.0650	0.0650	0.0650	0.0650	0.0675
Concn. found	—	—	3.10	3.10	3.10	3.10	3.10	3.23
% Rel. error			0	0	0	0	0	4.2
Chromium								
Absorbance	0.0357	0.1605	0.1035	0.1035	0.1035	0.1035	0.1057	0.1169
Concn. found	—	—	3.17	3.17	3.17	3.17	3.24	3.28
% Rel. error			0	0	0	0	2.2	3.5
Copper								
Absorbance	0.0438	0.2154	0.1325	0.1325	0.1325	0.1343	0.1367	0.1457
Concn. found	—	—	3.07	3.07	3.07	3.11	3.17	3.38
% Rel. error			0	0	0	1.3	3.3	10.1
Iron								
Absorbance	0.0128	0.0706	0.0424	0.0424	0.0424	0.0438	0.0438	0.0453
Concn. found	—	—	3.05	3.05	3.05	3.15	3.15	3.25
% Rel. error			0	0	0	3.3	3.3	6.6
Cadmium								
Absorbance	0.0701	0.2882	0.1824	0.1811	0.1811	0.1811	0.1811	0.1891
Concn. found	—	—	3.06	3.04	3.04	3.04	3.04	3.18
% Rel. error			0	0	0	0	0	4.6
Beryllium								
Absorbance	0.0218	0.0991	0.0540	0.0540	0.0540	0.0540	0.0535	0.0545
Concn. found	—	—	0.367	0.367	0.367	0.367	0.364	0.369
% Rel. error			0	0	0	0	0	0.5
Sodium								
Absorbance	0.0283	0.1244	0.0752	0.0768	0.0768	0.0752	0.0757	0.0899
Concn. found	—	—	0.295	0.302	0.302	0.295	0.297	0.356
% Rel. error			0	0	0	0	0	20.6
Calcium								
Absorbance	0.0482	0.2147	0.1379	0.1397	0.1391	0.1391	0.1421	0.1561
Concn. found	—	—	3.15	3.20	3.18	3.18	3.26	3.59
% Rel. error			0	1.6	0.94	0.94	3.5	14.0
Aspiration (cm^3 min^{-1})	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.4

Since the magnitude of absorption enhancement is dependent not only upon the metal involved but also upon the solvent system, it is apparent that each individual sample must be considered independently to determine if enhancement problems do exist.

One of the quickest and simplest means of detecting the presence of organic solvents is the determination of the total organic carbon (TOC) content of the sample. TOC instrumentation is available to many laboratories concerned with wastewater analyses. In this determination all organic compounds are burned to carbon dioxide which is determined by nondispersive infrared analysis. The total time required for most measurements is in the order of 2–4 min. This rapid technique can be used to determine the presence or absence of miscible organic solvents. Most instruments are calibrated in parts per million total carbon. A 0.5% solution of acetic acid will contain 0.20% carbon while a 0.5% ethyl acetate solution will contain 0.25% carbon. If the total organic carbon content is less than *ca.* 2,000 p.p.m., enhancement effects should be negligible. It should be pointed out that TOC will indicate the presence of any organic material and is not restricted to miscible solvents. A high TOC value in itself does not indicate that absorption enhancement will be present. However, if high TOC is indicated one should determine if enhancement is a factor to be considered.

If the presence of organic solvents is suspected above the 0.2% level, special precautions should be taken. Use of the "standard addition" technique will provide a safeguard against obtaining high values resulting from enhancement effects. If this approach is not desirable, one should at least spike the sample with a known amount of the analyte to determine if enhancement effects are significant.

For many years interference effects in atomic absorption were grossly overlooked. Today numerous references to interelement interferences can be found in the literature. It is also important to recognize the possible interferences that can be caused by the presence of organic solvents, even at relatively low concentrations. This is especially important when determining metals at trace concentrations in samples that can vary from day to day, not only in the type, but also in the concentration of organic solvent that may be present. Many wastewater streams fit this classification. Problems resulting from solvent enhancements can be eliminated if the analyst takes the simple precautions discussed above.

SUMMARY

The enhancing effect of organic solvents on atomic absorption determinations has been well established. The work described here was undertaken to determine the effects of low concentrations of miscible organic solvents on the determination of trace metals in water samples. The procedures used were those recommended for the determination of trace metals in industrial water effluents. The following elements were included: copper, chromium, cobalt, iron, cadmium, beryllium, sodium, and calcium. Solvents investigated were acetic acid, acetone, ethyl alcohol, and ethyl acetate. In all cases, no significant effect was found with organic solvent concentrations less than 0.5 % by volume. At organic solvent concentrations greater than 0.5 %, high results were obtained for some elements and solvent systems. Special precautions should be taken if the presence of miscible solvents is suspected.

RÉSUMÉ

Une étude est effectuée pour déterminer l'influence de faibles concentrations de solvants organiques sur le dosage par absorption atomique de traces de métaux dans l'eau. On utilise les méthodes recommandées pour l'analyse d'effluents industriels. On examine les éléments: cuivre, chrome, cobalt, fer, cadmium, béryllium, sodium et calcium; et les solvants: acide acétique, acétone, éthanol et acétate d'éthyle. Dans tous les cas, on n'observe aucune influence appréciable avec des solvants dont la concentration est inférieure à 0.5 %, en volume. Au-dessus de 0.5 %, on obtient dans certains cas des résultats trop forts. Des précautions spéciales devraient être prises, si l'on soupçonne la présence de solvants miscibles à l'eau.

ZUSAMMENFASSUNG

Der günstige Einfluss organischer Lösungsmittel auf Atomabsorptionsbestimmungen ist bekannt. Es wurde eine Untersuchung darüber ausgeführt, welchen Einfluss mischbare organische Lösungsmittel bei niedrigen Konzentrationen auf die Bestimmung von Spurenmetallen in wässrigen Proben haben. Die angewendeten Verfahren waren solche, die für die Bestimmung von Spurenmetallen in industriellen Abwässern empfohlen werden. Die Untersuchung umfasste folgende Elemente: Kupfer, Chrom, Kobalt, Eisen, Cadmium, Beryllium, Natrium und Calcium. Die untersuchten Lösungsmittel waren Essigsäure, Aceton, Äthylalkohol und Äthylacetat. In keinem Fall wurde ein signifikanter Einfluss bei Lösungsmittelkonzentrationen unterhalb 0.5 Vol.-% festgestellt. Bei Lösungsmittelkonzentrationen grösser als 0.5 Vol.-% wurden für einige Elemente und Lösungsmittelsysteme hohe Effekte beobachtet. Besondere Vorsichtsmassnahmen sollten getroffen werden, wenn mit der Gegenwart mischbarer Lösungsmittel zu rechnen ist.

REFERENCES

1 J. A. Dean and J. H. Lady, *Anal. Chem.*, 27 (1955) 1533.
2 R. Lockyer, J. E. Scott and S. Slade, *Nature*, 189 (1961) 831.
3 J. E. Allan, *Spectrochim. Acta*, 17 (1961) 467.
4 R. Belcher, R. M. Dagnall and T. S. West, *Talanta*, 11 (1964) 1257.
5 J. D. Winefordner, C. T. Mansfield and T. J. Vickers, *Anal. Chem.*, 35 (1963) 1607.
6 J. W. Robinson, *Atomic Absorption Spectroscopy*, Marcel Dekker, New York, 1966, p. 76.
7 C. L. Chakrabarti and S. P. Singhal, *Spectrochim. Acta*, 24B (1969) 663.
8 *Analytical Methods for Atomic Absorption Spectrophotometry*, Perkin-Elmer, Norwalk, Conn.
9 *Standard Methods for the Examination of Water and Wastewater*, 13th Ed., Published by the American Public Health Association, 1015, 18th Street, N.W., Washington, D. C. 20036, 1971.

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THE DETERMINATION OF MICRO AMOUNTS OF POLYTHIONATES

PART VI.* SPECTROPHOTOMETRIC DETERMINATION OF ULTRAMICRO AMOUNTS OF TETRA-, PENTA- AND HEXATHIONATE BY CYANOLYSIS AND SOLVENT EXTRACTION

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In previous papers[1-3] of this series, the reaction of polythionates (tetra-, penta- and hexathionate) with cyanide has been described in detail and methods for the determination of the polythionate when tetra-, penta- or hexathionate alone is present have been presented. These methods are based on the formation of thiocyanate from polythionates by the following reaction:

$$S_xO_6^{2-}+(x-1)CN^-+H_2O=S_2O_3^{2-}+SO_4^{2-}+2HCN+(x-3)SCN^- \quad (1)$$
$$(x=4,\ 5 \text{ and } 6)$$

and on photometric determination of the thiocyanate thus formed with iron(III). In other work[4], a new spectrophotometric method for the determination of thiocyanate in the range $2.0\cdot10^{-7}$–$1.0\cdot10^{-5}$ *M*, based on the extraction of a complex formed between methylene blue and thiocyanate with an organic solvent, has been developed.

The present paper is concerned with the spectrophotometric determination of ultramicro amounts of polythionates; the method is based on the formation of thiocyanate equivalent to tetra-, penta- and hexathionate, and on the extraction of the methylene blue–thiocyanate complex with dichloroethane. It has proved possible to increase the sensitivity of the methods for the determination of polythionates by *ca.* 60-fold. The proposed method appears to be more sensitive than any previous method for polythionates. Conditions suitable for the simultaneous determination of the three polythionates have been established.

EXPERIMENTAL

Apparatus

Spectrophotometric measurements were made with a Shimazu model QV-50 spectrophotometer with 10-mm glass cells.

Extractions were done with an Iwaki model KM shaker. pH measurements were made with a Hitachi-Horiba model M-5 pH meter. Temperatures were regulated by a Taiyo model M-1 thermostat.

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* Part V: *Bull. Chem. Soc. Jap.*, 39 (1966) 703.

Chemicals

All other chemicals used besides polythionates were of an analytical grade and were used without further purification.

Polythionates. Potassium tetrathionate was prepared as described by Stamm *et al.*[5], and potassium pentathionate and potassium hexathionate as described by Goehring and Feldmann[6]. The raw polythionates obtained were recrystallized and then dried at room temperature before storage at −10° ±2°. The water physically adsorbed on the polythionates and the water of crystallization of pentathionate were estimated by the Karl Fischer method. It was confirmed that the polythionates were pure enough for the present purpose; the purity of the polythionates was estimated by determining their total potassium and sulfur contents[1-3]. Standard polythionate solutions were stored at 5° ±2°.

Standard solutions

Standard tetrathionate solution, $1.0 \cdot 10^{-3}$ *M*. Dissolve 151.3 mg of potassium tetrathionate (water content 0.07%) in redistilled water, and dilute to 500 ml. Prepare working standards by suitable dilution.

Standard pentathionate solution, $1.0 \cdot 10^{-3}$ *M*. Dissolve 186.8 mg of potassium pentathionate (water content including water of crystallization 10.48%) in redistilled water, and dilute to 500 ml. Prepare working standards by appropriate dilution.

Standard hexathionate solution, $1.0 \cdot 10^{-3}$ *M*. Dissolve 183.8 mg of potassium hexathionate (water content 0.29%) in redistilled water, and dilute to 500 ml. Prepare working standards by suitable dilution.

Standard thiocyanate solution. Dissolve potassium thiocyanate in redistilled water, and standardize by Volhard's method. Prepare working solutions by appropriate dilution. These standards were used to ascertain whether or not the reaction of polythionates with cyanide went to completion and was stoichiometric.

Reagents

Sodium cyanide solution. Prepare working cyanide solutions by suitable dilutions of a 2 *M* solution.

Buffer solutions. Prepare sodium dihydrogenphosphate–sodium hydroxide (0.2 or 0.4 *M*) solutions for pH adjustment.

Methylene blue solution, $8.0 \cdot 10^{-3}$ *M*. Dissolve 760 mg of methylene blue (98.5%) in redistilled water, and dilute to 250 ml. Dilute this stock solution as required.

Recommended procedure

Add 1.5 ml of 0.04 *M* sodium cyanide solution, 0.5 ml of phosphate buffer solution (0.2 *M*), pH 6.0, and then 10.0 ml of sample solution to a 50-ml volumetric flask; the pH of the solution is thereby brought to a value of 7.4. Place the flask in a thermostat at 40° for at least 4.5 h, to convert the polythionates quantitatively to thiocyanate. Add 1.0 ml of 0.12 *M* formaldehyde solution, and transfer the mixture to a 50-ml separatory funnel. To this mixture, add 1.5 ml of $2.0 \cdot 10^{-3}$ *M* methylene blue solution and 10.0 ml of dichloroethane. Shake for about 2 min, to extract the complex formed between methylene blue and thiocyanate. When the two layers have separated, transfer the organic layer to a 15-ml glass tube equipped with a glass stopper, and add some anhydrous sodium sulfate. Shake the mixture vigorously by hand until transparent, and measure the absorbance of the clear solution against dichloroethane at 657 nm[4].

RESULTS AND DISCUSSION

Calibration curves

The calibration curves shown in Fig. 1 were obtained as described above, with standard solutions of thiocyanate and polythionates ($x = 4, 5$ and 6). The graphs show a good linear relationship. According to eqn. (1), when one mole of polythionate undergoes cyanolysis, $(x-3)$ moles of thiocyanate are formed. Therefore, if polythionate is converted to thiocyanate stoichiometrically and completely, the calibration curves of tetra-, penta- and hexathionate should be respectively once, twice and three times as sensitive as that of thiocyanate when plotted as molar concentrations. Figure 1 proves that all three polythionates are quantitatively converted to thiocyanate according to eqn. (1). It was also confirmed that the calibration curves are in exact accordance with that of thiocyanate when the concentration scales for thiocyanate and tetrathionate, and pentathionate, are drawn to one-third and two-thirds, respectively, of the scale of hexathionate concentration.

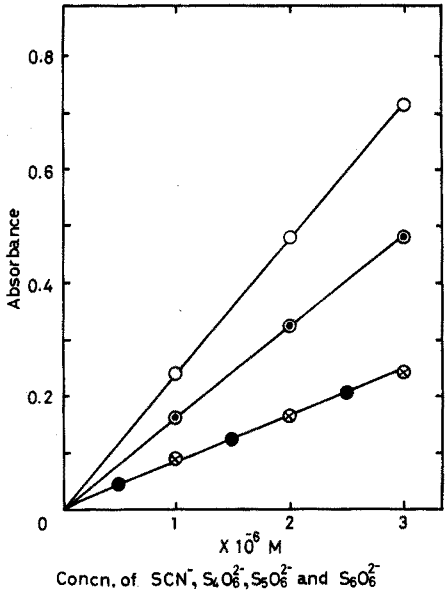


Fig. 1. Calibration curves (reagent blank subtracted). (●) Thiocyanate; (⊗) tetrathionate; (⊙) pentathionate; (○) hexathionate.

Effect of pH on the cyanolysis of polythionates

With regard to the cyanolysis of polythionates in amounts such as 10^{-4} *M*, it has been observed[1-3] that tetra-, penta- and hexathionate do not undergo partial alkaline decomposition at lower pH values than 12.1, 8.8 and 8.9, respectively. In the present study, the reaction of polythionates with cyanide was carried out at various pH values below 8.5. The experimental results (reagent blank subtracted) are listed in Table I; there are considerable differences in absorbance between thiocyanate and pentathionate or hexathionate at the pH levels of 8.5 and 8.1, respectively, which indicates that partial alkaline decomposition of the polythionates occurs even at these pH levels. Table I shows that the cyanolysis of pentathionate and hexathionate must be done at a lower pH value than 7.6. It was also made clear that tetrathionate undergoes partial alkaline decomposition above pH 11.0; its cyanolysis must be performed below pH 10.8. These results, which differ from the previous papers[1-3], may be attributed to the fact that the amount of polythionates undergoing alkaline decomposition is small but almost independent of the amount of polythionates concerned. The small amounts of tetra-, penta- and hexathionate which undergo alkaline decomposition within the pH ranges of 11.0–12.1, 7.8–8.8 and 7.8–8.9, respectively, could not be detected by the previous procedure, but could be checked by the present highly sensitive method.

TABLE I

EFFECT OF pH ON THE CYANOLYSIS OF POLYTHIONATES

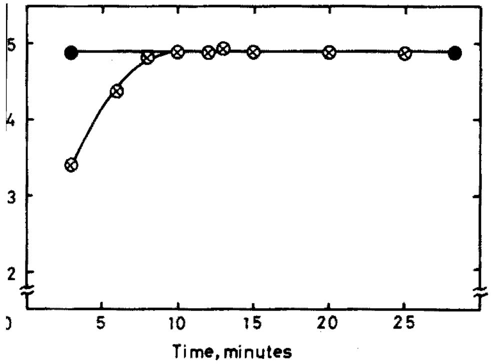
pH	*Absorbance*[a]							
	SCN$^-$ 6.0·10^{-6} *M*		$S_4O_6^{2-}$ 6.0·10^{-6} *M*		$S_5O_6^{2-}$ 3.0·10^{-6} *M*		$S_6O_6^{2-}$ 2.0·10^{-6} *M*	
7.4	0.488	0.483	0.482	0.491	0.476	0.476	0.483	0.488
7.6	0.482	0.486	0.486	0.486	0.468	0.477	0.482	0.472
8.1	0.486	0.484	0.491	0.491	0.448	0.440	0.442	0.457
8.5	0.479	0.491	0.491	0.486	0.413	0.419	0.433	0.425

[a] Concentration, pH and volume of buffer solutions employed were not always the same, so the absorbances of polythionates for each pH value should be compared with those of thiocyanate for the same pH.

An object of the present study was to determine polythionates in mixtures with one another; an attempt was therefore made to establish conditions under which all three polythionates were simultaneously and stoichiometrically converted to thiocyanate. It was confirmed that the optimal pH ranges for the reactions of tetra-, penta- and hexathionate with cyanide are, respectively, 7.2–10.8, 7.2–7.6 and 7.2–7.6 under the conditions of the above recommended procedure. Accordingly, it was concluded that all three polythionates can be determined sensitively by the same procedure when the pH value is within the range 7.2–7.6.

Rate of cyanolysis of polythionates

Figure 2 shows the rate of cyanolysis of tetrathionate at 40° and pH 10.8. In this case, 0.5 ml of a 0.02 *N* sodium hydroxide solution was employed in place of 0.5 ml of buffer solution (pH 6.0) in the recommended procedure, in order to adjust the pH to 10.8. The maximal absorbance corresponding to stoichiometric cyanolysis of tetrathionate was reached in 10 min. The higher the pH of the solution, the more rapid the rate of cyanolysis; therefore it is desirable that the procedure should be carried out at as high a pH level as possible, provided that it is below 10.8. However, since pentathionate and hexathionate undergo partial alkaline decomposition above pH 7.8, pH values below 7.6 were used.



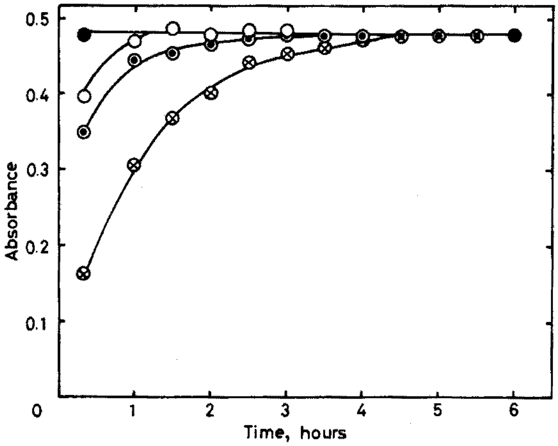


Fig. 2. Rate of cyanolysis of tetrathionate at 40° and pH 10.8 (reagent blank subtracted). (●) $6.0 \cdot 10^{-6}$ *M* SCN^-; (⊗) $6.0 \cdot 10^{-6}$ *M* $S_4O_6^{2-}$.

Fig. 3. Rate of cyanolysis of polythionates at 40° and pH 7.4 (reagent blank subtracted). (●) $6.0 \cdot 10^{-6}$ *M* SCN^-; (○) $2.0 \cdot 10^{-6}$ *M* $S_6O_6^{2-}$; (⊙) $3.0 \cdot 10^{-6}$ *M* $S_5O_6^{2-}$; (⊗) $6.0 \cdot 10^{-6}$ *M* $S_4O_6^{2-}$.

Figure 3 shows the rate of cyanolysis of the polythionates at 40° and pH 7.4. It can be seen that the reactions of tetra-, penta- and hexathionate went to completion in 4.5, 3.5 and 1.5 h respectively, and thereafter gave constant absorbances. Accordingly, the reaction time must exceed 4.5 h for complete cyanolysis of all three polythionates. It was also concluded from Figs. 2 and 3 that the reaction time of polythionates can be shortened from 4.5 h to 3.7 h by leaving the reaction solution for 3.5 h at pH 7.4, and then for 10 min at pH 10.8, after 1.0 ml of 1.0 *M* ammonia had been added to increase the pH.

Reaction temperature

In order to accelerate the rate of cyanolysis, the reaction temperature was raised from 40° to higher temperatures, the mixture solution being allowed to stand for 4.5 h in each case. The results are listed in Table II. Tetrathionate was stoichiometrically converted to thiocyanate even at 60°; no thermal decomposition occurred.

TABLE II

EFFECT OF TEMPERATURE ON THE CYANOLYSIS OF POLYTHIONATES

Temp. (°)	*Absorbance*[a]							
	SCN^- $6.0 \cdot 10^{-6}$ *M*		*$S_4O_6^{2-}$* $6.0 \cdot 10^{-6}$ *M*		*$S_5O_6^{2-}$* $3.0 \cdot 10^{-6}$ *M*		*$S_6O_6^{2-}$* $2.0 \cdot 10^{-6}$ *M*	
40	0.489	0.487	0.482	0.491	0.476	0.488	0.483	0.488
45	0.488	0.483	0.488	0.493	0.473	0.461	0.473	0.473
50	0.479	0.481	0.477	0.483	0.453	0.456	0.456	0.456
60	0.492	0.477	0.482	0.489	0.433	0.451	0.451	0.444

[a] The reagent blank was subtracted.

Pentathionate and hexathionate gave lower absorbances at 50° and 60°, because of thermal decomposition. Even at 45°, they seemed to undergo a slight thermal decomposition in addition to cyanolysis, so the reaction temperature was fixed at 40°.

Effect of amount of sodium cyanide

In measuring the effect of the amount of sodium cyanide on the conversion of tetra-, penta- and hexathionate to thiocyanate, 0.5, 1.0 and 1.5 ml of 0.04 *M* cyanide solution were employed; in all cases the solutions were buffered to pH 7.2–7.6. Cyanolysis of the polythionates was incomplete with 0.5 and 1.0 ml of 0.04 *M* cyanide solution, but when 1.5 ml was used, the calibration curves of all three polythionates were linear and coincided exactly with that of standard thiocyanate when plotted as equivalent concentrations.

Masking of the excess of cyanide with formaldehyde

The cyanide used for the cyanolysis of polythionates interfered with the proposed method; both the reagent blank and the methylene blue–thiocyanate complex showed quite high absorbances. Accordingly, an attempt was made to mask the excess of cyanide with formaldehyde. Figure 4 shows how the cyanide could be masked by increasing the amount of formaldehyde added. The absorbances for both the reagent blank and the complex remained constant over the range 0.10–0.20 *M* formaldehyde. Consequently, 1.0 ml of 0.12 *M* formaldehyde was used to mask the excess of cyanide.

Effect of amount of methylene blue

It is obvious that the formation of extractable species may be affected by the

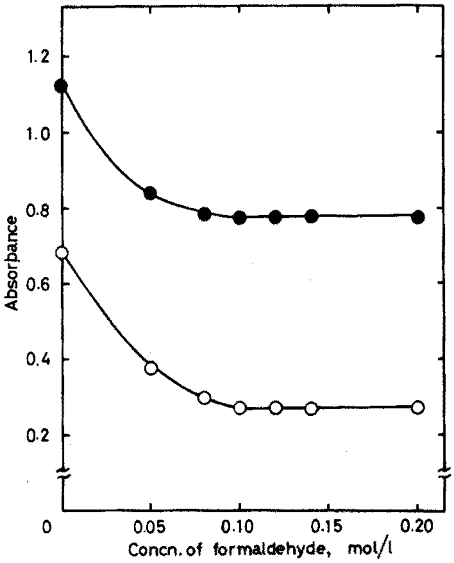


Fig. 4. Masking of excess of cyanide with formaldehyde. The volume of formaldehyde solution employed was 1.0 ml. (○) Reagent blank, (●) $6.0 \cdot 10^{-6}$ *M* SCN^-.

concentration of methylene blue. In order to establish the optimal amount, 1.0, 1.5 and 2.0 ml of $2.0 \cdot 10^{-3}$ *M* methylene blue solution were added to a solution containing standard thiocyanate and certain amounts of cyanide, buffer and formaldehyde; the extraction was then done as described above. All the resulting calibration curves formed parallel straight lines, hence 1.5 ml of $2.0 \cdot 10^{-3}$ *M* methylene blue solution was employed.

Effect of diverse ions

The effect of diverse ions was investigated under the conditions of the recommended procedure; the experiments were made on aqueous solutions containing various amounts of diverse ions, both in the presence of $6.0 \cdot 10^{-6}$ *M* thiocyanate, $6.0 \cdot 10^{-6}$ *M* tetrathionate, $3.0 \cdot 10^{-6}$ *M* pentathionate and $2.0 \cdot 10^{-6}$ *M* hexathionate, and in their absence. The experimental results are given in Table III. Obviously anions cause much more serious interference than cations. Copper(II) interferes seriously, probably, because of the formation of a complex between copper(I) cyanide and methylene blue. Bromide, iodide, nitrate and perchlorate interfere with the determination of polythionates, when present in amounts corresponding to that of polythionates. Interference of sulfide seems to be due to the formation of thiocyanate as a result of its reaction with cyanide.

TABLE III

EFFECT OF DIVERSE IONS

Ion	*Added as*	*Concn. (p.p.m.)*	*Absorbance*				
			Reagent blank	*SCN^-* $6.0 \cdot 10^{-6}$ *M*	*$S_4O_6^{2-}$* $6.0 \cdot 10^{-6}$ *M*	*$S_5O_6^{2-}$* $3.0 \cdot 10^{-6}$ *M*	*$S_6O_6^{2-}$* $2.0 \cdot 10^{-6}$ *M*
None		0	0.273	0.767	0.757	0.765	0.757
Na^+	$Na_2SO_4 \cdot 10H_2O$	1000	0.249	0.741	0.736	0.736	0.731
NH_4^+	$(NH_4)_2SO_4$	1000	0.239	0.752	0.748	0.748	0.738
K^+	K_2SO_4	1000	0.258	0.767	0.750	0.750	0.743
Mg^{2+}	$MgSO_4$	500	0.263	0.741	0.743	0.748	0.738
Zn^{2+}	$ZnSO_4 \cdot 7H_2O$	100	0.287	0.784	0.633	0.762	0.762
Mn^{2+}	$MnSO_4 \cdot 7H_2O$	100	0.315	0.797	0.743	0.782	0.787
Fe^{2+}	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	100	0.250	0.738	0.533	0.686	0.686
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	100	>1.200	>1.200	>1.200	>1.200	>1.200
Al^{3+}	$Al_2(SO_4)_3 \cdot 18H_2O$	100	0.281	0.769	0.540	0.689	0.712
Fe^{3+}	$NH_4Fe(SO_4)_2 \cdot 12H_2O$	100	0.245	0.690	0.502	0.688	0.747
F^-	NaF	10	0.265	0.789	0.759	0.772	0.747
Cl^-	NaCl	10	0.319	0.793	0.793	0.791	0.785
Br^-	KBr	1	0.313	0.785	0.785	0.775	0.775
I^-	KI	0.1	0.796	>1.200	>1.200	>1.200	>1.200
ClO_4^-	$KClO_4$	0.1	0.372	0.889	0.873	0.863	0.863
NO_3^-	KNO_3	1	0.487	0.910	0.896	0.896	0.903
SO_4^{2-}	Na_2SO_4	1000	0.245	0.745	0.745	0.731	0.726
$S_2O_3^{2-}$	$Na_2S_2O_3 \cdot 5H_2O$	1	0.272	0.772	0.765	0.777	0.760
S^{2-}	$Na_2S \cdot 9H_2O$	10	>1.200	>1.200	>1.200	>1.200	>1.200

SUMMARY

A spectrophotometric determination of ultramicro amounts of tetra-, penta- and hexathionate is proposed. The method is based on extraction of a complex formed between methylene blue and thiocyanate (equivalent to the polythionates) with dichloroethane, and measurement of the absorbance of the organic phase. The conditions for all three polythionates to be completely converted into thiocyanate were established by varying the pH, temperature, reaction time, and amount of cyanide. The method is suitable for the determination of $3.3 \cdot 10^{-7}$–$1.0 \cdot 10^{-5}$ *M* tetrathionate, $1.7 \cdot 10^{-7}$–$5.0 \cdot 10^{-6}$ *M* pentathionate, and $1.0 \cdot 10^{-7}$–$3.3 \cdot 10^{-6}$ *M* hexathionate.

RESUME

On propose une méthode spectrophotométrique pour un dosage ultramicro de tétra-, penta- et hexathionate. Elle est basée sur l'extraction d'un complexe formé entre bleu de méthylène et thiocyanate (équivalent aux polythionates), dans le dichloroéthane; on mesure l'absorption de la phase organique. On examine les conditions nécessaires pour la transformation complète des trois polythionates en thiocyanate, en faisant varier pH, température, durée de réaction et quantité de cyanure. Cette méthode convient au dosage de tétrathionate de $3.3 \cdot 10^{-7}$–$1.0 \cdot 10^{-5}$ *M*, de pentathionate de $1.7 \cdot 10^{-7}$–$5.0 \cdot 10^{-6}$ *M* et d'hexathionate de $1.0 \cdot 10^{-7}$–$3.3 \cdot 10^{-6}$ *M*.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode zur Bestimmung von Ultramikromengen Tetra-, Penta- und Hexathionat vorgeschlagen. Sie beruht auf der Bildung eines Komplexes zwischen Methylenblau und mit den Polythionaten äquivalentem Thiocyanat, Extraktion des Komplexes mit Dichloräthan und Messung der Extinktion der organischen Phase. Die Bedingungen, unter denen alle drei Polythionate vollständig in Thiocyanat umgewandelt werden, wurden durch Variation von pH-Wert, Temperatur, Reaktionszeit und Cyanidmenge festgestellt. Die Methode eignet sich für die Bestimmung von $3.3 \cdot 10^{-7}$–$1.0 \cdot 10^{-5}$ *M* Tetrathionat, $1.7 \cdot 10^{-7}$–$5.0 \cdot 10^{-6}$ *M* Pentathionat und $1.0 \cdot 10^{-7}$–$3.3 \cdot 10^{-6}$ *M* Hexathionat.

REFERENCES

1 T. Koh, *Bull. Chem. Soc. Jap.*, 38 (1965) 1510.
2 T. Koh and I. Iwasaki, *Bull. Chem. Soc. Jap.*, 38 (1965) 2135.
3 T. Koh and I. Iwasaki, *Bull. Chem. Soc. Jap.*, 39 (1966) 352.
4 T. Koh and I. Iwasaki, *Bull. Chem. Soc. Jap.*, 40 (1967) 569.
5 H. Stamm, M. Goehring and U. Feldmann, *Z. Anorg. Allgem. Chem.*, 250 (1942) 226.
6 M. Goehring and U. Feldmann, *Z. Anorg. Chem.*, 257 (1948) 223.

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ETUDE DU SYNERGISME DANS L'EXTRACTION DU COBALT(II) PAR LE MELANGE OXYDE DE (CARBOXY-2-ETHYL) DIPHENYLPHOSPHINE–4-(3-PHENYLPROPYL) PYRIDINE EN SOLUTION DANS LE CHLOROFORME

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(Reçu le 23 avril 1972)

Nous avons vu dans une précédente publication[1] que l'oxyde de (carboxy-2-éthyl)diphénylphosphine (CEDPPO ou HA) en extraction liquide–liquide de cations métalliques, donnait lieu, pour des pH faiblement acides, à une complexation des cations en phase aqueuse. Nous montrons dans cette étude que malgré une très forte complexation aqueuse sous la forme CoA_6^{4-}, le cobalt (II) peut être extrait quantitativement en phase organique sous la forme CoA_3, HA, 3B par addition de 4-(3-phényl-propyl)pyridine (43PPP ou B) au système CEDPPO–chloroforme. Le choix de conditions expérimentales convenables permet de résoudre graphiquement le système, d'identifier les complexes présents dans chacune des deux phases aqueuse et organique et de donner les valeurs des constantes d'équilibre correspondantes.

ÉTUDE THÉORIQUE DE L'EXTRACTION

Nous supposons que le CEDPPO et la 43PPP agissent simultanément sur le cobalt(II) pour ne donner qu'un seul complexe hydrophobe. Nous admettons de plus qu'aux concentrations en cobalt(II) auxquelles nous avons travaillé, le complexe est sous forme monomère en phase organique[2]. Dans ces conditions, ce complexe peut être représenté par la formule tout à fait générale $(CoA_2, (n-2)HA, uB)_o$ et l'équilibre d'extraction est alors:

$$Co_a^{2+} + \frac{n}{2} H_2A_{2_o} + uB_o \rightleftarrows (CoA_2, (n-2)HA\ , uB)_o + 2H^+$$

sachant que les indices a et o désignent respectivement les phases aqueuse et organique et que le CEDPPO (HA) existe principalement sous forme de dimère[3] dans le chloroforme. La constante d'équilibre d'extraction K_{ex} est alors:

$$K_{ex} = \frac{[CoA_2, (n-2)HA, uB]_o \cdot [H^+]^2}{[Co^{2+}]_a \cdot [H_2A_2]_o^{\frac{1}{2}n} \cdot [B]_o^u}$$

Si nous tenons compte de la complexation en phase aqueuse sous la forme $CoA_x^{(x-2)-}$ selon l'équilibre:

$$Co_a^{2+} + xA_a^- \rightleftarrows CoA_{xa}^{(x-2)-}$$

dont la constante d'équilibre de formation β_{CoA_x} est donnée par:

$$\beta_{\mathrm{CoA}_x} = \frac{[\mathrm{CoA}_x^{(x-2)-}]_\mathrm{a}}{[\mathrm{Co}^{2+}]_\mathrm{a} \cdot [\mathrm{A}^-]_\mathrm{a}^x}$$

et si nous négligeons les complexes hydroxylés du cobalt(II)[4], la concentration du cobalt en phase aqueuse est donnée par:

$$[\mathrm{Co}]_\mathrm{a} = [\mathrm{Co}^{2+}]_\mathrm{a} + [\mathrm{CoA}_x^{(x-2)-}]_\mathrm{a} = [\mathrm{Co}^{2+}]_\mathrm{a}(1+\beta_{\mathrm{CoA}_x} \cdot [\mathrm{A}^-]_\mathrm{a}^x)$$

Nous exprimons $[\mathrm{A}^-]_\mathrm{a}$ en fonction de K_a, constante de dissociation du CEDPPO en phase aqueuse, et de $[\mathrm{HA}]_\mathrm{a}$. Nous obtenons ainsi la relation:

$$[\mathrm{Co}]_\mathrm{a} = [\mathrm{Co}^{2+}]_\mathrm{a}(1+\beta_{\mathrm{CoA}_x} K_\mathrm{a}^x \cdot [\mathrm{HA}]_\mathrm{a}^x \cdot [\mathrm{H}^+]^{-x})$$

Nous appelons D_M le coefficient de partage du cobalt(II) entre chacune des deux phases organique et aqueuse et α_{MA_x} l'expression:

$$1+\beta_{\mathrm{CoA}_x} K_\mathrm{a}^x [\mathrm{HA}]_\mathrm{a}^x [\mathrm{H}^+]^{-x}$$

Nous obtenons alors les deux relations:

$$\log D_\mathrm{M} = \log K_\mathrm{ex} + \tfrac{1}{2} n \log [\mathrm{H_2A_2}]_\mathrm{o} + u \log [\mathrm{B}]_\mathrm{o} - \log \alpha_{\mathrm{CoA}_x} + 2\,\mathrm{pH} \qquad (1)$$

$$\log \alpha_{\mathrm{CoA}_x} = \log (1+\beta_{\mathrm{CoA}_x} K_\mathrm{a}^x [\mathrm{HA}]_\mathrm{a}^x [\mathrm{H}^+]^{-x}) \qquad (2)$$

qui tiennent compte d'une part de l'extraction en phase organique d'un complexe $\mathrm{CoA_2}$, $(n-2)\mathrm{HA}$, $u\mathrm{B}$, et d'autre part d'une complexation en phase aqueuse sous la forme $\mathrm{CoA}_x^{(x-2)-}$. Il s'agit donc de déterminer les valeurs de x, u, n, K_ex et β_{CoA_x}. Nous exposons ci-dessous la méthode utilisée, si ces différentes étapes sont compatibles avec nos résultats expérimentaux, nous vérifions par là même nos hypothèses de travail.

La concentration en $(\mathrm{H_2A_2})_\mathrm{o}$ *reste constante*

La relation (1) montre que $\log D_\mathrm{M} - 2\,\mathrm{pH}$ n'est fonction que de $u \log [\mathrm{B}]_\mathrm{o} - \log \alpha_{\mathrm{CoA}_x}$. Ainsi à pH constant, $\log \alpha_{\mathrm{CoA}_x}$ qui n'est fonction que de $\log [\mathrm{HA}]_\mathrm{a} + \mathrm{pH}$ reste constant et si nous faisons varier $[\mathrm{B}]_\mathrm{o}$, la courbe correspondante $\log D_\mathrm{M} - 2\,\mathrm{pH} = \mathrm{f}(\log [\mathrm{B}]_\mathrm{o})$ doit être une droite de pente u.

Ainsi pour différentes valeurs du pH, nous devons obtenir un réseau de droites de pente u, chacune d'entre elles correspondant à une valeur déterminée de $\log \alpha_{\mathrm{CoA}_x}$.

Si nous traçons alors une verticale qui coupe ce réseau, les points d'intersection ainsi obtenus sont tels que $\log [\mathrm{B}]_\mathrm{o}$ est constant et la relation (1) montre que les ordonnées de ces points sont telles que:

$$\log \alpha_{\mathrm{CoA}_x} - C = 2\,\mathrm{pH} - \log D_\mathrm{M}$$

C étant une constante égale dans ces conditions à $\log K_\mathrm{ex} + \frac{1}{2}n \log [\mathrm{H_2A_2}]_\mathrm{o} + u \log [\mathrm{B}]_\mathrm{o}$. Chaque droite correspondant à une valeur de $\log [\mathrm{HA}]_\mathrm{a} + \mathrm{pH}$ déterminé, nous pouvons porter d'après la relation (2):

$$2\,\mathrm{pH} - \log D_\mathrm{M} = \log \alpha_{\mathrm{CoA}_x} - C = \mathrm{f}(\log [\mathrm{HA}]_\mathrm{a} + \mathrm{pH})$$

Toujours dans le cadre de nos hypothèses, cette courbe doit alors être une courbe théorique normalisée du type $\log Y = \log (1+X^x) = \mathrm{f}(\log X)$ qui admet deux asymptotes: l'une horizontale et l'autre oblique de pente x.

Nous déterminons ainsi les valeurs de u, x et β_{CoA_x}.

La concentration en $(H_2A_2)_o$ *varie*

Nous pouvons tracer d'après la relation (1):

$$\log D_M - 2\,\mathrm{pH} + \log \alpha_{\mathrm{CoA}_x} - u \log[\mathrm{B}]_o = \mathrm{f}(\log[\mathrm{H_2A_2}]_o)$$

et la courbe obtenue doit être une droite de pente $n/2$ permettant la détermination de n et de K_{ex}.

CONDITIONS EXPÉRIMENTALES

Les extractions sont étudiées à 25° entre 10 cm^3 de chacune des deux phases aqueuse et organique.

Nous préparons différentes solutions de 43PPP et de CEDPPO dans le chloroforme à des concentrations convenables par pesées. La phase organique est obtenue par addition de deux solutions, l'une de 43PPP et l'autre de CEDPPO et elle est éventuellement ajustée à 10 cm^3 par addition de chloroforme pur.

Nous préparons également différentes solutions aqueuses, tamponnées aux pH désirés, de force ionique fixée à 0.5 par du nitrate de sodium, de concentration convenable en nitrate de cobalt(II) et marquées à l'isotope cobalt-60. Les tampons utilisés sont des mélanges phtalate acide de potassium–soude[5]. L'isotope cobalt-60, émetteur γ d'énergies 1.17 et 1.33 MeV, et de période 5.3 ans, nous est fourni par le Commissariat à l'Energie Atomique de Saclay (France) sous forme de chlorure en solution dans 0.8 cm^3 d'acide chlorhydrique, d'activité totale 5.28 mCi et d'activité spécifique 76 mCi mg^{-1}. Les dosages sont effectués après 3 h d'agitation et 30 min de décantation, par comptages de 5 cm^3 de chacune des deux phases aqueuse et organique, à l'aide d'un appareil Intertechnique Didac 800—Sonde NaI activé au Tl.

RÉSULTATS

Vérifications préliminaires

Nous vérifions tout d'abord que le CEDPPO et la 43PPP séparément n'extraient pratiquement pas le cobalt(II). Les essais sont effectués pour une concentration initiale en cobalt(II) égale à $10^{-5}\,M$.

CEDPPO seul. Pour une concentration en CEDPPO de $3 \cdot 10^{-1}\,M$, nous constatons qu'à des pH de 4.01, 4.61, 5.20 et 5.80, l'extraction reste toujours inférieure à 3%.

Nous obtenons des résultats identiques pour un pH de 5.20 lorsque la concentration en CEDPPO est de $7.80 \cdot 10^{-2}\,M$, $1.46 \cdot 10^{-1}\,M$ et $3.66 \cdot 10^{-1}\,M$.

43PPP seule. En l'absence de $\mathrm{NaNO_3}$, pour une concentration en 43PPP égale à $5 \cdot 10^{-2}\,M$, l'extraction reste inférieure à 7% pour des pH de 4.01, 4.61, 5.20 et 5.80.

Avec une même concentration en 43PPP et un pH de 5.80, l'addition de quantités croissantes de $\mathrm{NaNO_3}$ ne provoque aucun changement. L'extraction en effet reste inférieure à 7% pour des concentrations en $\mathrm{NaNO_3}$ de $10^{-1}\,M$, $2 \cdot 10^{-1}\,M$, $3 \cdot 10^{-1}\,M$, $4 \cdot 10^{-1}\,M$ et $5 \cdot 10^{-1}\,M$.

Nous obtenons les mêmes résultats pour une concentration en $\mathrm{NaNO_3}$ de $5 \cdot 10^{-1}\,M$ et un pH de 5.80, lorsque la concentration de la 43PPP varie de $2.02 \cdot 10^{-2}\,M$ à $5.1 \cdot 10^{-1}\,M$.

Nous voyons ainsi que l'extraction du cobalt(II) par le CEDPPO ou la 43PPP reste toujours très faible et nous admettons dans la suite de cette étude qu'il n'existe pas d'extractions parasites venant se superposer au synergisme.

Etude à $[H_2A_2]_o$ *constante*

Détermination de u. Nous fixons des concentrations initiales en CEDPPO et en cobalt(II) égales respectivement à $10^{-1}M$ et à $5 \cdot 10^{-6}M$. Pour des pH égaux à 4.01, 4.20, 4.40, 4.50, 4.56 et 4.61, nous faisons varier la concentration initiale en 43PPP entre les valeurs extrêmes de $4.04 \cdot 10^{-4}M$ et $5.05 \cdot 10^{-3}M$. De telles concentrations non seulement sont favorables au synergisme mais de plus présentent les avantages suivants:

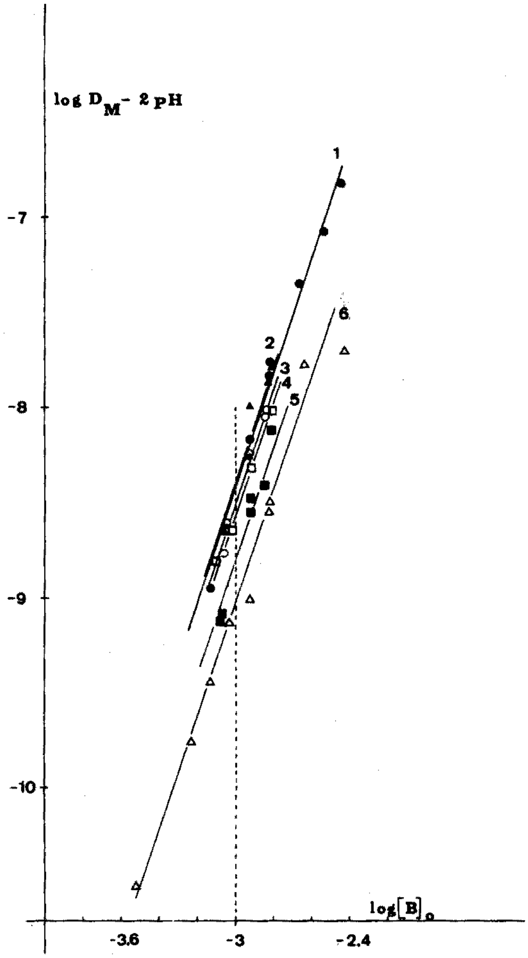

Fig. 1. Détermination de *u*. Courbes donnant $\log D_M - 2\,\text{pH} = f(\log[B]_o)$ à pH constant égal à (1) 4.01; (2) 4.20; (3) 4.40; (4) 4.50; (5) 4.56 et (6) 4.61.

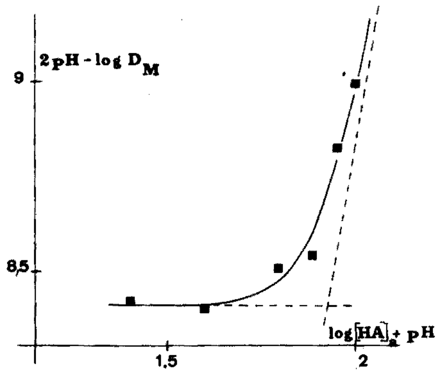

Fig. 2. Détermination de *x*. Courbe donnant $2\,\text{pH} - \log D_M = f(\log[HA]_a + \text{pH})$ pour $[B]_o = 10^{-3}M$. (——) Courbe théorique normalisée du type $\log Y = \log(1 + X^6) = f(\log X)$.

La concentration en cobalt (II) est faible et l'espèce extraite en phase organique est monomère[2].

La formation du complexe extrait dans le chloroforme ne modifie ni les concentrations initiales en 43PPP et en CEDPPO, ni la valeur du pH initialement fixé.

La concentration en CEDPPO est très supérieure à celle de la 43PPP si bien que, lorsque cette dernière varie de $4.04 \cdot 10^{-4} M$ à $5.05 \cdot 10^{-3} M$, la formation du complexe mixte CEDPPO–43PPP[6] ne perturbe pas la concentration initiale en $(H_2A_2)_o$. De cette façon, $\log [H_2A_2]_o$ garde une valeur constante lorsque le pH reste constant et il en est de même pour $\log [HA]_a$.

Lorsque le pH varie de 4.01 à 4.61, le calcul montre que $\log [H_2A_2]_o$ prend des valeurs comprises entre 1.60 et 1.62.

Dans ces conditions nous voyons que $\log [H_2A_2]_o$ garde une valeur pratiquement constante quels que soient le pH et la concentration en 43PPP utilisés. La relation (2) précédente montre de plus qu'à pH constant, $\log \alpha_{CoA_x}$ n'est pas modifié par la variation de la concentration en 43PPP puisque $\log [HA]_a + pH$ reste constant. Par contre, les concentrations en 43PPP à l'équilibre ne sont pas identiques à celles initiales, car ces dernières sont modifiées par la formation du complexe mixte entre le CEDPPO et la 43PPP. Elles sont alors recalculées à l'aide des constantes correspondantes.

Nous avons porté ainsi, d'après la relation (1), $\log D_M - 2\,pH = f(\log [B]_o)$ pour chacune des valeurs de pH comprises entre 4.01 et 4.61. La Figure 1 montre que les courbes obtenues sont des droites de pente 3. Nous pouvons déjà envisager que le complexe organique extrait de la forme $(CoA_2, (n-2)HA, uB)_o$ est unique et nous pouvons attribuer à u une valeur égale à 3.

Détermination de x et de β_{CoA_x}. A chacune de ces droites correspond une valeur de $\log [HA]_a + pH$ bien définie que le calcul permet de déterminer[6]. Pour une verticale définie par $\log [B]_o = -3$ et d'après les relations (1) et (2) précédentes, nous portons les valeurs obtenues $2\,pH - \log D_M$ en fonction de $\log [HA]_a + pH$. La Figure 2 montre qu'aux points expérimentaux obtenus, nous pouvons adapter une courbe théorique normalisée du type $\log Y = \log (1 + X^6) = f(\log X)$ qui admet deux asymptotes: l'une horizontale et l'autre oblique de pente 6.

Le cobalt (II) est ainsi complexé en phase aqueuse sous la forme CoA_6^{4-} dont la constante d'équilibre de formation, déterminée par l'intersection des deux asymptotes est donnée par une valeur de $\log \beta_{CoA_x}$ égale à 13.1 ± 0.1.

Etude à $[H_2A_2]_o$ variable: détermination de n et de K_{ex}

Pour une concentration initiale en 43PPP égale à $2.02 \cdot 10^{-3} M$ et un pH de 4.40, nous faisons varier la concentration initiale en CEDPPO de $10^{-1} M$ à $4 \cdot 10^{-2} M$. Connaissant u, x et $\log \beta_{CoA_x}$, nous pouvons porter, d'après la relation (1), $\log D_M - 2\,pH - 3 \log [B]_o + \log \alpha_{CoA_x} = f(\log [H_2A_2]_o)$. La Figure 3 montre que la courbe obtenue est une droite dont la pente donne pour n une valeur de 3, et dont l'ordonnée à l'origine permet la détermination K_{ex}.

Le cobalt(II) est ainsi extrait en phase organique sous la forme CoA_2, HA, 3B et nous obtenons pour la constante d'équilibre d'extraction une valeur $\log K_{ex}$ égale à 3.0 ± 0.1.

Courbes d'extraction du cobalt (II) en fonction du pH

Nous avons représenté sur la Figure 4 les courbes d'extraction du cobalt (II)

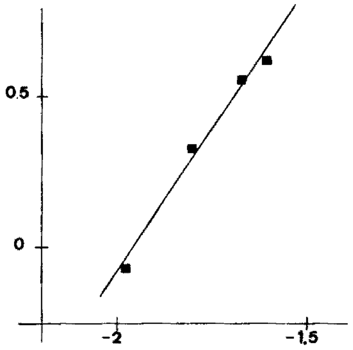

Fig. 3. Détermination de *n*. Courbe donnant log D_M-2 pH -3 log $[B]_o+\log\alpha_{CoA_x}=f(\log[H_2A_2]_o)$.

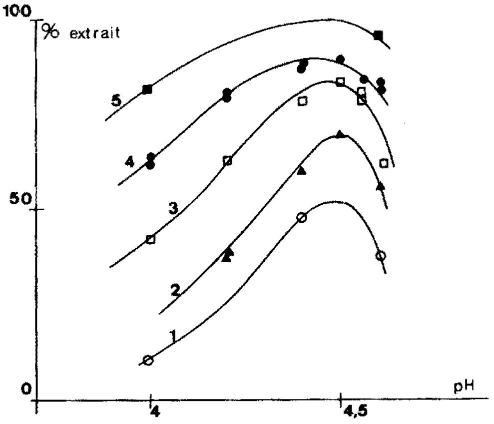

Fig. 4. Courbes d'extraction du Co(II) en fonction du pH pour une concentration initiale en CEDPPO de $10^{-1}M$ et pour des concentrations initiales en 43PPP égales à (1) $1.01\cdot10^{-3}M$; (2) $1.21\cdot10^{-3}M$; (3) $1.62\cdot10^{-3}M$; (4) $2.02\cdot10^{-3}M$; (5) $3.03\cdot10^{-3}M$.

en fonction du pH, pour une concentration en CEDPPO égale à $10^{-1}M$ et pour différentes concentrations initiales en 43PPP comprises entre $1.01\cdot10^{-3}M$ et $3.03\cdot10^{-3}M$. Nous constatons que si le pouvoir d'extraction de la 43PPP ou celui du CEDPPO est très faible vis-à-vis du cobalt, ce dernier peut être quantitativement extrait en phase organique par une combinaison convenable de ces deux agents.

RÉSUMÉ

Les auteurs ont montré que le cobalt(II) était fortement complexé par le CEDPPO sous la forme CoA_6^{4-} dans des phases aqueuses de pH supérieurs à 4, et que son extraction dans la phase organique était rendue, de ce fait, pratiquement nulle. Ils ont déterminé la valeur de la constante de formation de ce complexe. Ils ont montré que l'addition de 4-(3-phénylpropyl)pyridine exaltait cette extraction pour la rendre pratiquement quantitative sous certaines conditions expérimentales, par la formation en phase organique d'un complexe CoA_2, HA, 3B dont la valeur de la constante d'équilibre d'extraction est également déterminée.

SUMMARY

The synergistic effect of (carboxy-2-ethyl)diphenylphosphine oxide (HA) in the presence of 4-(3-phenylpropyl)pyridine (B) in the extraction of cobalt(II) is described. The cobalt can be extracted in the form CoA_2, HA, 3B, despite complex formation in the aqueous phase involving the species CoA_6^{4-}. The extraction constant and formation constant are given.

ZUSAMMENFASSUNG

Der synergetische Effekt von (Carboxy-2-äthyl)diphenylphosphinoxid (HA)

in Gegenwart von 4-(3-Phenylpropyl)pyridin (B) bei der Extraktion von Kobalt(II) wird beschrieben. Das Kobalt kann in der Form CoA_2, HA, 3B extrahiert werden, obwohl sich in der wässrigen Phase der starke Komplex CoA_6^{4-} bildet. Die Extraktionskonstante und die Bildungskonstante werden angegeben.

BIBLIOGRAPHIE

1 J. L. Rocca et M. Porthault, *Anal. Chim. Acta*, 55 (1971) 341.
2 N. Tanaka, N. Nakasuka et S. Sasane, *Solvent Extraction Chemistry*, North-Holland, Amsterdam, 1967, p. 154.
3 J. L. Rocca et M. Porthault, *Bull. Soc. Chim. Fr.*, 5 (1970) 2036.
4 A. Ringbom, *Les Complexes en Chimie Analytique*, Dunod, Paris, 1967, pp. 330–37.
5 R. G. Bates, *Determination of pH*, Wiley, New-York, 1964, p. 157.
6 J. L. Rocca, O. Vittori et M. Porthault, *Anal. Chim. Acta*, 61 (1972) 247.

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COMPLEX FORMATION OF THORIUM WITH XYLENOL ORANGE PHOTOMETRIC INVESTIGATION OF MH_jL_n AND MH_nL_{n+1} SYSTEMS

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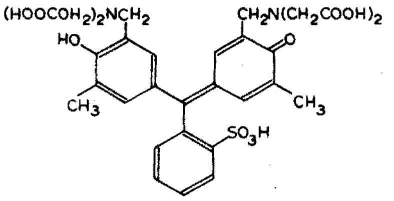
Xylenol orange (I) is an excellent compleximetric indicator and photometric reagent for about 50 metal ions[1]. The composition of its metal complexes and their stability has been a puzzle because of the two chelating systems for about a decade. The differences in the results obtained by various authors are caused mainly by the inadequate purity of the xylenol orange used. Recently[2] a convenient method of purification was found, so that the problems of composition and stability of complexes can be solved.



(I)

EXPERIMENTAL

Apparatus

All photometric measurements were made with a Gilford Spectrophotometer, Model 2400 (Oberlin, Ohio). Quartz cells of 1 cm pathlength were used. An Orion Model 801 pH-meter (A. H. Thomas Co., Philadelphia, Pa.), with a glass and calomel electrode pair, was used for pH measurements.

Reagents

Xylenol orange (K&K Laboratories, Inc., Plainview, N.Y.) was purified as described by Murakami *et al.*[2]. The product was analyzed with the following results: 55.1% C, 4.9% H, 4.3% N, 4.7% S; required for $C_{31}H_{32}N_2O_{13}S$: 55.3% C, 4.8% H, 4.2% N, 4.8% S. Paper chromatography was performed in the system of *n*-butanol–aqueous 1 *M* ammonia (1 : 5) with Whatman paper No. 1 at 25°. The R_F value was 0.90 (red spot); the product used was chromatographically pure.

The stock solutions of thorium perchlorate and xylenol orange were $1.00 \cdot 10^{-3}$ *M*. The concentration of thorium was checked by titration with EDTA. The pH was adjusted by means of perchloric acid and hexamine. The ionic strength was kept constant (0.10 *M*) by means of sodium perchlorate. All chemicals were "Baker-Analyzed" reagents.

Procedure

The sequence of buffer, xylenol orange and thorium perchlorate was adhered to during the preparation of all solutions. Dilutions were made with solutions containing the same concentration of the buffer as the solution diluted. The temperature was kept at 25 ± 1°. The absorbance of solutions was measured against a buffer blank after 15 min.

THEORETICAL

Limits of the reagent concentration and pH

Usually the composition and stability of the main complex MH_jL_n of a polydentate colored ligand L can be determined. Owing to the stepwise complex formation, it can be assumed that employing an excess of the ligand and higher pH (than the optimum of formation of MH_jL_n) another complex of MH_hL_{n+1} will be obtained.

If c_M and c_L are the total concentrations of the metal and ligand respectively and $c_L \gg c_M$, then:

$$c_L = [L]\alpha_{L(H)} \tag{1}$$

where $\alpha_{L(H)}$ is the coefficient of side reactions of the ligand L and hydrogen ions. Then the necessary concentration of c_L to have 99% of the metal in the complex will be

$$c_{L(\min)} = \alpha_{L(H)}\{100/(\beta_n[H]^j)\}^{1/n} \tag{2}$$

where β_n is the overall stability constant of the complex MH_jL_n.

If a higher pH and the concentration of c_L given by eqn. (2) are used, the question of the highest pH with negligible metal ion hydrolysis arises. Since every metal hydrolysis is initiated by the formation of the complex of M(OH) with the stability constant

$$\beta^* = [M(OH)][H][M]^{-1} \tag{3}$$

the limiting can be defined as 1% formation of the complex M(OH) of the total metal concentration, so that

$$100[M(OH)] = c_M = 100\beta^*[M][H]_{\lim}^{-1} \tag{4}$$

On the other hand, from eqn. (2):

$$c_M\alpha^n_{L(H)}/([M][H]^j_{\lim}c^n_L) = \beta_n \tag{5}$$

The combination of eqns. (4) and (5) gives for the limiting pH

$$\mathrm{pH}_{\lim} = \frac{1}{j+1}\log \beta_n c^n_L/(100\beta^*\alpha^n_{L(H)}) \tag{6}$$

Composition and stability of MH_hL_{n+1}

Taking into account the values of c_L and $\mathrm{pH}_{\lim}$ given by eqns. (2) and (6), respectively, we can write

$$c_M = [MH_jL_n] + [MH_hL_{n+1}] = K_n[M]c_L^n + K_{n+1}[M]c_L^{n+1} \tag{7}$$

where the effective constants are

$$K_n = \beta_n[H]^j\alpha_{L(H)}^{-n}, \quad K_{n+1} = \beta_{n+1}[H]^h\alpha_{L(H)}^{-n-1} \tag{8ab}$$

If each component of the system can absorb the radiation, the effective absorbance will be

$$\Delta A = \Delta\varepsilon_n[MH_jL_n] + \Delta\varepsilon_{n+1}[MH_hL_{n+1}] = \Delta\varepsilon_n K_n[M]c_L^n + \Delta\varepsilon_{n+1}K_{n+1}[M]c_L^{n+1} \tag{9}$$

where

$$\Delta A = A - A_L \tag{10}$$

The effective molar absorptivities are given by

$$\Delta\varepsilon_n = \varepsilon_n - n\varepsilon_L, \quad \Delta\varepsilon_{n+1} = \varepsilon_{n+1} - (n+1)\varepsilon_L \tag{11ab}$$

A and A_L are the measured absorbances of the complexing system and of the reagent solution, respectively; ε_n, ε_{n+1} and ε_L are the molar absorptivities of the complexes MH_jL_n, MH_hL_{n+1} and of the reagent, respectively. The absorbance of the metal ion is always negligible because of its small concentration.

The combination of eqns. (7) and (9) results in

$$\Delta A/(c_M\Delta\varepsilon_n) = (K_n + kK_{n+1}c_L)/(K_n + K_{n+1}c_L) \tag{12}$$

where

$$k = \Delta\varepsilon_{n+1}/\Delta\varepsilon_n \tag{13}$$

Performing the dilution of the solution, *i.e.* using another pair of concentrations

$$c'_M = c_M/2 \text{ and } c'_L = c_L/2 \tag{14ab}$$

we have instead of eqn. (12)

$$2\Delta A'/(c_M\Delta\varepsilon_n) = (2K_n + kK_{n+1}c_L)/(2K_n + K_{n+1}c_L) \tag{15}$$

Combining eqns. (12) and (15) by elimination of k, we obtain a normalized function

$$y = 1/(x-1) - 1 \tag{16}$$

where after substitution from eqn. (8ab)

$$y = K_{n+1}c_L/K_n = \beta_{n+1}[H]^{h-j}c_L/(\beta_n\alpha_{L(H)}) \tag{17}$$

and

$$x = (\Delta A - \Delta\varepsilon_n c_M)/(2\Delta A' - \Delta\varepsilon_n c_M) \tag{18}$$

Obviously the value of y can be only a positive number. Therefore it must be $1 < x < 2$. Dependence of log y *vs.* x is given in Table I. If the value of x is calculated from experimental results, the corresponding value of log y can be found from Table I. If that value is determined for different pH values, the true value of log β_{n+1} will exhibit smallest deviations for true value of h (the values of j and log β_n are known). In this way the composition of the complex MH_hL_{n+1} and its overall stability constant can be determined. The whole procedure can be advantageously programmed for a computer. The value of $\Delta\varepsilon_{n+1}$ is calculated by means of eqns. (12) and (13).

TABLE I

DEPENDENCE OF LOG y ON x

x	$\log y$		x	$\log y$		x	$\log y$	
1.01	2.00	1.99	1.18	0.66	1.82	1.35	0.27	1.65
1.02	1.69	1.98	1.19	0.63	1.81	1.36	0.25	1.64
1.03	1.51	1.97	1.20	0.60	1.80	1.37	0.23	1.63
1.04	1.38	1.96	1.21	0.58	1.79	1.38	0.21	1.62
1.05	1.28	1.95	1.22	0.55	1.78	1.39	0.19	1.61
1.06	1.19	1.94	1.23	0.53	1.77	1.40	0.18	1.60
1.07	1.12	1.93	1.24	0.50	1.76	1.41	0.16	1.59
1.08	1.06	1.92	1.25	0.48	1.75	1.42	0.14	1.58
1.09	1.00	1.91	1.26	0.45	1.74	1.43	0.12	1.57
1.10	0.95	1.90	1.27	0.43	1.73	1.44	0.11	1.56
1.11	0.91	1.89	1.28	0.41	1.72	1.45	0.09	1.55
1.12	0.86	1.88	1.29	0.39	1.71	1.46	0.07	1.54
1.13	0.83	1.87	1.30	0.37	1.70	1.47	0.05	1.53
1.14	0.79	1.86	1.31	0.35	1.69	1.48	0.04	1.52
1.15	0.75	1.85	1.32	0.33	1.68	1.49	0.02	1.51
1.16	0.72	1.84	1.33	0.31	1.67	1.50	0.00	1.50
1.17	0.69	1.83	1.34	0.29	1.66			
	$-\log y$	x		$-\log y$	x		$-\log y$	x

The dependence of $\log y$ on x presented in Table I indicates that most accurate results are obtained in the area of $\log y = 0$, $x = 1.5$. It is usually possible to reach that area by a convenient selection of pH. However, this cannot be accomplished if the stabilities of complexes MH_jL_n and MH_hL_{n+1} are similar. In that case, the right side of eqn. (17) cannot reach the value of 1 because of the limits of c_L and pH. For $h = j = 0$, usually $5 < \log \beta_{n+1}/\beta_n < 8$. If

$$\Delta A = 2\Delta A' \tag{19}$$

for a broad spectral range ($\Delta\lambda > 30$ nm), it indicates that only one complex either MH_jL_n or MH_hL_{n+1} is formed. The former case will occur if $\Delta A = \Delta\varepsilon_n c_M$. The latter case indicates that procedures for only one complex can be used. If the relationship of eqn. (19) is valid for a narrow spectral range ($\Delta\lambda \sim 20$ nm), then in that range, $\Delta\varepsilon_n \approx \Delta\varepsilon_{n+1}$. Obviously, those values of ΔA and $\Delta A'$ cannot be used for calculation of x since $x \to 0/0$ and the eqns. (7) and (9) are identical.

If the value of c_L is kept constant and only c_M is varied, then instead of eqn. (15), the following equation is obtained:

$$2\Delta A'/(c_M \Delta\varepsilon_n) = (K_n + kK_{n+1}c_L)/(K_n + K_{n+1}c_L) \tag{20}$$

Thus after combination with eqn. (12) eqn. (19) is again obtained, indicating that that procedure cannot be used for the given purpose.

Composition and stability of M_2H_sL

In the case of xylenol orange, it is also necessary to determine the composition and stability of the complex of M_2H_sL in the presence of MH_jL. The procedure is similar to that indicated above. However, $c_M \gg c_L$ and the minimum metal concentration for the highest acidity is given by

$$c_{M(\mathrm{min})} = 100\alpha_{L(H)}/(\beta_1 [H]^j) \tag{21}$$

An equation analogous to eqn. (16) is obtained:

$$y^* = 1/(x^* - 1) - 1 \tag{22}$$

where

$$y^* = K_{21} c_M \,/\, K_1 = \beta_{21} [H]^{s-j} c_M/\beta_1 \tag{23}$$

and

$$x^* = (\Delta A^* - \Delta\varepsilon_1 c_L)/(2\Delta A^{*\prime} - \Delta\varepsilon_1 c_L) \tag{24}$$

Analogous symbols are designated by asterisks; K_{21} and β_{21} are the effective and overall stability constants of the complex M_2H_sL. Table I can be used again.

RESULTS AND DISCUSSION

Figure 1 shows the possibilities of complex formation between thorium and xylenol orange with molar ratios of 1 : 1, 1 : 2 and 2 : 1. Since the structure of xylenol orange does not exclude the formation of a 2 : 2 complex, the problem of dimerization was investigated by the method of stoichiometric dilution[3]. The results obtained are collected in Table II; they indicate the formation of a 1 : 1 complex.

By estimating the effective stability constant (again employing the stoichiometric dilution) at different pH values, it was possible to determine the composition

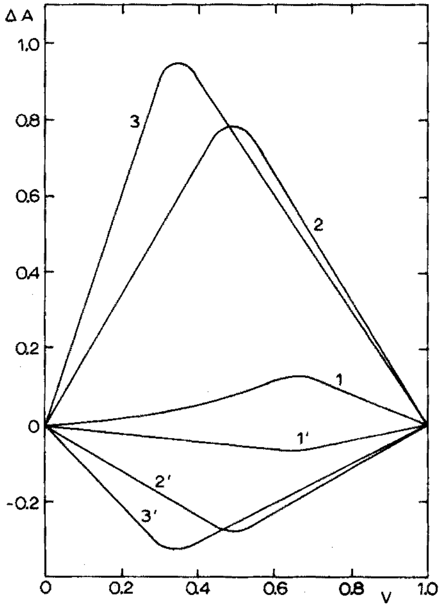


Fig. 1. Continuous variation of Th^{4+}–xylenol orange: (1, 1′) pH 1.10, 560 and 430 nm; (2, 2′) pH 2.46, 575 and 430 nm; (3, 3′) pH 5.80, $c_{NH_4F} = 3.20 \cdot 10^{-3}$ M, 568 and 430 nm. $v = c_{Th}/(c_{Th} + c_L)$. $c_{Th} + c_L = 4.00 \cdot 10^{-5}$ M throughout.

TABLE II

DETERMINATION OF THE REAL MOLAR RATIO Th:XO IN THE MAIN COMPLEX[a]

$-\log c_M$	x	$-\log y_{11}$	$\log K_{11}$	$-\log y_{22}$	$\log K_{22}$
4.10	1.015	2.71	6.81	6.12	18.42
4.40	1.027	2.40	6.80	5.33	18.53
4.70	1.039	2.10	6.80	4.73	18.83
5.00	1.052	1.82	6.82	4.22	19.22
5.30	1.072	1.55	6.85	3.77	19.67

[a] pH 2.18, $\lambda = 565$ nm; x, y_{11} and y_{22} are the normalized functions of the stoichiometric dilution method[3], K_{11} and K_{22} are the effective stability constants of the monomer and dimer respectively.

TABLE III

DETERMINATION OF THE COMPOSITION AND LOGARITHMIC OVERALL STABILITY CONSTANT OF THE COMPLEX ThH_2L[a]

pH	x	$-\log y_{11}$	$\log K_{11}$	$\log \alpha_{L(H)}$	$\log \beta_1$
1.82	1.187	0.73	5.43	25.82	34.89
2.18	1.039	2.10	6.80	23.81	34.97
2.46	1.018	2.62	7.32	22.68	34.92

[a] $-\log c_M = 4.70$, $\lambda = 565$ nm; logarithmic overall stability constants of hydrogen complexes of xylenol orange: 12.23 (HL), 22.58 (H_2L), 29.28 (H_3L), 32.13 (H_4L), 34.45 (H_5L), 35.85 (H_6L), 34.81 (H_7L), 32.98 (H_8L), 29.66 (H_9L)[2].

and stability constant of the complex MH_jL by means of the equation[4]:

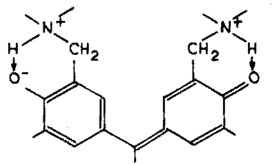
$$\log K_{11}\alpha_{L(H)} + j\text{pH} = \log \beta_1 \tag{25}$$

The results obtained are presented in Table III.

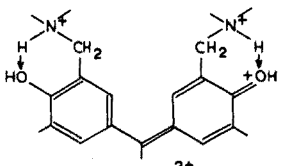
Then by means of eqns. (2), (6) and (21), it was possible to calculate the minimum total concentration of the ligand ($-\log c_{L(\min)} = 4.76$ for pH 2.18), the limiting pH of 10.8 (for $-\log c_L = 3.22$ and $\log \beta^* = -4.23$)[5] and the minimum total concentration of thorium ($-\log c_{M(\min)} = 3.48$ for pH 1.82).

After those data had been obtained, the composition and stability of complexes of MH_hL_2 and M_2H_sL were investigated by the procedure described in the theoretical part. The results found are collected in Tables IV and V.

Since it is very difficult to isolate individual complexes in a convenient solid form, their structure was investigated by comparison with hydrogen complexes. Rehak, Körbl[6] and Murakami *et al.*[2] have found that the bathochromic species of xylenol orange hydrogen complexes have the structure



H_2L^{4-}



H_8L^{2+}

TABLE IV

DETERMINATION OF THE COMPOSITION AND LOGARITHMIC OVERALL STABILITY CONSTANT OF THE COMPLEX ThH_4L_2[a]

λ (nm)	$\Delta\varepsilon_1 \cdot 10^{-3}$ ($cm^2\ mmole^{-1}$)	x	log y	log $\alpha_{L(H)}$	log β_2
pH 2.46					
560	36.41	1.945	−1.24	22.68	64.51
570	38.30	1.959	−1.37	22.68	64.38
580	32.10	1.935	−1.16	22.68	64.59
pH 2.93					
560	36.39	1.666	−0.30	20.62	64.33
570	38.28	1.563	−0.11	20.62	64.52
580	32.07	1.618	−0.21	20.62	64.42
pH 3.52					
560	36.33	1.148	0.76	18.66	64.61
570	38.22	1.232	0.52	18.66	64.37
580	32.02	1.183	0.65	18.66	64.50

[a] $-\log c_M = 4.40$, $-\log c_L = 3.22$.

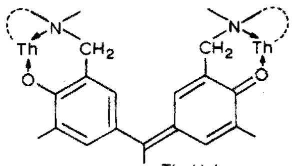
TABLE V

DETERMINATION OF THE COMPOSITION AND LOGARITHMIC OVERALL STABILITY CONSTANT OF THE COMPLEX Th_2H_2L[a]

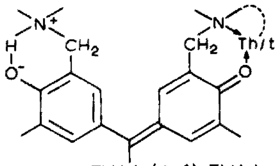
λ (nm)	$\Delta\varepsilon_1 \cdot 10^{-3}$ ($cm^2\ mmole^{-1}$)	x^*	log y^*	log β_{21}
pH 1.54				
570	38.35	1.090	1.00	39.10
580	32.10	1.050	1.28	39.38
590	21.83	1.078	1.07	39.17
pH 1.82				
570	38.35	1.066	1.15	39.25
580	32.10	1.052	1.26	39.36
590	21.83	1.086	1.03	39.13
pH 2.18				
570	38.35	1.047	1.31	39.41
580	32.10	1.062	1.18	39.28
590	21.83	1.075	1.09	39.19

[a] $-\log c_M = 3.17$, $-\log c_L = 4.40$.

Both species H_2L^{4-} and H_8L^{2+} exhibit typical delocalization of π-electrons in the system of $O-(C_6H_4)-C=(C_6H_4)=O$. A similar delocalization can be expected for complexes Th_2H_2L, ThH_2L and ThH_4L_2 since they also are bathochromic species. If the inert gas electronic configuration of thorium(IV) is considered, the following structures can be assumed:



Th_2H_2L



ThH_2L ($t = 1$), ThH_4L_2 ($t = 2$)

TABLE VI

AVERAGE MOLAR ABSORPTIVITIES AND LOGARITHMIC OVERALL STABILITY CONSTANTS

Complex	$\varepsilon \cdot 10^{-3}$ *(cm² mmole⁻¹) (λ, nm)*	*log β*	*log β′*[a]
H_2L[b]	60.90 ± 0.40 (578)	22.58 ± 0.10	—
H_8L[b]	65.40 ± 1.50 (515)	32.98 ± 0.39	—
ThH_2L	36.54 ± 0.41 (560) 38.95 ± 0.41 (570) 32.10 ± 0.41 (580)	34.93 ± 0.08	12.35 ± 0.08
ThH_4L_2	55.75 ± 0.83 (560) 62.63 ± 0.82 (570) 64.33 ± 0.84 (580)	64.47 ± 0.09	19.31 ± 0.09
Th_2H_2L	44.83 ± 0.98 (570) 25.10 ± 0.76 (580) 7.62 ± 0.75 (590)	39.25 ± 0.11	9.71 ± 0.11

[a] $\beta' = [M_m H_{nj} L_n][M]^{-m}[H_j L]^{-n}$. [b] Data determined by Murakami *et al.*[2].

A comparison of average molar absorptivities and stability constants of individual species is given in Table VI. The differences existing may be well explained by the extent of π-electron delocalization. The values of molar absorptivity were calculated by means of the equation:

$$k = [1 + \Delta A/(c_M \Delta\varepsilon_n) - x]/(2 - x) \tag{26}$$

which was obtained as a result of the combination of eqns. (12), (15) and (18). The reported values of overall stability constants refer to macroscopic constants[7].

The stepwise formation of Th_2H_2L, ThH_2L and ThH_4L_2 by increasing the pH is in agreement with the relationship of optimal acidity of complex formation and the composition of the particular complex[4]. The non-existence of the dimer of $Th_2(H_rL)_2$ is given by different acidities of both oxygens in $O\text{–}(C_6H_4)\text{–}C{=}(C_6H_4){=}O$ and by stereochemical and statistical factors.

Some authors[8,9] explain complex formation with xylenol orange only by aminodiacetic acid groups. The formation of mononuclear complexes can be explained thus, but not the spectra of the complexes.

In addition, it may be noted that the approach outlined can also be used for investigation of mixed complexes of $MY_iH_jL_n$ and $MY_gH_hL_{n+1}$. It is necessary to have $c_Y \gg c_M$ so that $[Y] = c_Y/\alpha_{Y(H)}$. The values of i and g are determined by varying the concentration c_Y at constant acidity.

This work was aided by a grant from the National Research Council, Ottawa, Ont., which is greatly appreciated.

SUMMARY

A simple procedure is described for photometric investigations of systems of two metal–ligand complexes where the ligand is absorbing and polydentate. The procedure was used to study the complex formation between thorium and xylenol orange. The complexes of ThH_2L, ThH_4L_2 and Th_2H_2L were found with logarithmic overall stability constants of 34.93 ± 0.08, 64.47 ± 0.09, 39.25 ± 0.11, and molar absorptivities of 38,950 ± 410, 62,630 ± 820 and 44,830 ± 980 cm^2 $mmole^{-1}$ (for 570 nm), respectively.

RÉSUMÉ

On décrit une méthode simple pour l'examen photométrique de systèmes de deux complexes métal–ligand. Elle a été appliquée à l'étude de formation de complexes entre thorium et xylénol orange. Les complexes suivants: ThH_2L, ThH_4L_2 et Th_2H_2L ont été décelés, avec des constantes de stabilité logarithmiques de 34.93 ± 0.08, 64.47 ± 0.09, 39.25 ± 0.11 respectivement, et des coefficients d'extinction molaires de 38,950 ± 410, 62,630 ± 820 et 44,830 ± 980 cm^2 $mmole^{-1}$ (pour 570 nm).

ZUSAMMENFASSUNG

Es wird ein einfaches Verfahren für photometrische Untersuchungen von Systemen zweier Metall–Ligand-Komplexe beschrieben, bei denen der Ligand absorbiert und vielzähnig ist. Das Verfahren wurde auf die Untersuchung der Komplexbildung zwischen Thorium und Xylenolorange angewendet. Die logarithmischen Gesamt-Stabilitätskonstanten der Komplexe ThH_2L, ThH_4L_2 und Th_2H_2L wurden zu 34.93 ± 0.08, 64.47 ± 0.09 und 39.25 ± 0.11 ermittelt, die zugehörigen molaren dekadischen Extinktionskoeffizienten bei 570 nm sind 38950 ± 410, 62630 ± 820 und 44830 ± 980 cm^2 $mmol^{-1}$.

REFERENCES

1 B. W. Budesinsky, in H. A. Flaschka and A. J. Barnard, Jr., *Chelates in Analytical Chemistry*, Vol. 1, Marcel Dekker, New York, 1967, p. 15.
2 M. Murakami, T. Yoshino and S. Harasawa, *Talanta*, 14 (1967) 1293.
3 B. W. Budesinsky, *J. Inorg. Nucl. Chem.*, 31 (1969) 1345.
4 B. W. Budesinsky, *Z. Anal. Chem.*, 207 (1965) 247.
5 L. G. Sillen and A. E. Martell, *Stability Constants of Metal-Ion Complexes*, Suppl. No. 1, Chem. Society, London, 1971, p. 19.
6 B. Rehak and J. Körbl, *Collect. Czech. Chem. Commun.*, 25 (1960) 797.
7 M. T. Beck, *Chemistry of Complex Equilibria*, Van Nostrand Reinhold, London, 1970, p. 158.
8 P. V. Marchenko, *Ukr. Khim. Zh.*, 30 (1964) 224.
9 A. K. Mukherji, *Talanta*, 13 (1966) 1183.

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THE CHEMICAL CHARACTERIZATION OF SILICON–GERMANIUM THERMOELECTRIC ALLOYS

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During the 1950's, the thermoelectric properties of semiconductors received wide attention. A number of materials with outstanding thermoelectric properties were considered, among them PbTe, BiTe, SiMo, GeTe, SbTe, and SiGe. Although each of these has its advantages, the silicon–germanium alloys emerge as leading candidates because they operate in air as well as vacuum, they have outstanding mechanical properties, and they are useful at high temperatures[1].

Silicon–germanium alloys containing between 60 and 80 at.-% silicon have received a major share of the attention. Phosphorus is the most common dopant (*ca.* 0.3 wt.-%) used in n-type SiGe, and boron (*ca.* 0.1 wt.-%) is the most common p-type dopant; in both cases, the selection of the dopant is largely dependent on the solid solubility of the element in the alloy.

Production of homogeneous material is difficult, and the chemical composition is sensitive to process variables. Because material performance is strongly affected by these compositional variations, and, in addition, is highly dependent on dopant concentrations, definition of the chemical composition is important. This paper describes analytical methods for determining silicon, germanium, phosphorus, and boron in SiGe thermoelectrics. Other techniques for making these determinations have been reported in the literature; the methods described here represent original adaptions of standard or classical analytical methods to this problem.

GERMANIUM

Most chemical methods used for the accurate determination of germanium in SiGe alloys require separation of germanium from silicon and from most dopants and impurities. Cheng and Goydish[2] determined germanium in pure SiGe alloys by volatilizing the silicon as the tetrafluoride in the presence of citric acid, evaporating the sample to dryness, and igniting to the oxide at 850–900°. This technique is obviously limited by the impurity level of the material. Other separations, such as precipitation of germanium as the sulfide and volatilization of germanium as the tetrachloride, are suitable but require extreme care in order to achieve 100% separation and recovery. Current ion-exchange procedures for germanium involve adsorption of the chloride or fluoride complexes from strong acid solutions; this requires ion-exchange apparatus which is resistant to hydrofluoric acid, and presents problems such as loss of germanium by volatilization of the halide.

A new analytical procedure for the determination of germanium in SiGe alloys, based on the titration of a germanium–mannitol complex[3] with sodium hydroxide after an ion-exchange separation of the germanium, is proposed here. The SiGe is dissolved by alkali fusion, the solution is diluted to give a *ca.* 1 *M* sodium hydroxide solution, and germanium is quantitatively retained on a column containing Amberlite XE-243 ion-exchange resin. Silicon is not held by the resin. The germanium is subsequently eluted with 1 *M* nitric acid and determined by the mannitol–sodium hydroxide titration. Although boron behaves in exactly the same manner as the germanium, it is normally present at *ca.* 0.1 % which is within the experimental error of the determination.

Experimental

Reagents. Amberlite XE-243 ion-exchange resin (Rohm and Haas Company, Philadelphia) and germanium metal powder (−325 mesh, 99.999 % purity, Alfa Inorganics, Beverly, Mass.) were used. All other reagents and chemicals were of A. R. quality.

Apparatus. The borosilicate glass ion-exchange columns were 30 × 1 cm (i.d.) and each contained a coarse fritted glass disc to retain the resin, and stopcocks to control the flow rate.

The germanium–mannitol titrations were done with a Sargent-Welch Recording Titrator, Model DG, with a Sargent combination glass–calomel electrode to monitor the pH during the titration.

Preparation and regeneration of ion-exchange columns. Because gas evolves during the initial contact of the resin with concentrated acid, the resin was equilibrated with 3 *M* hydrochloric acid before being put into columns. The resin was back-washed with water in the column and allowed to settle under a slight back-pressure of water. Hydrochloric acid (50 ml of 3 *M*) was passed through the column, followed by water until the effluent was neutral. An equal amount of 3 *M* ammonia solution was then passed through the column, followed by flushing with water until the effluent was neutral.

The same procedure was used in regenerating the columns after each separation procedure. The columns were run at maximum flow rate (2–3 ml min^{-1}) during the pretreatment and regeneration steps.

Procedure.

Weigh a sample containing 30–60 mg of germanium into a zirconium crucible along with 2 g of sodium hydroxide pellets. Cover the crucible with a nickel lid, put on a hot plate at room temperature, and heat to the maximum temperature of the hot plate (550°) until all visible reaction ceases. (Caution: The fusion of SiGe alloy releases hydrogen gas which may ignite violently if the initial fusion is done over a flame.) Then heat the crucible over a Meker burner until a clear melt is obtained. Dissolve the product of the fusion in water, dilute to *ca.* 50 ml, and transfer to the ion-exchange column. Pass the sample through the column at a flow rate of 1–2 ml min^{-1}. Wash the column with 50 ml of 0.1 *M* sodium hydroxide at the same flow rate to elute the remaining silicon, and then wash with water until the effluent is neutral.

Elute the germanium with 100 ml of (1 + 9) nitric acid at the same flow rate, followed by 50 ml of water. Neutralize the effluent with 50 % sodium hydroxide, acidify to a methyl red end-point with the nitric acid, and boil for 2–3 min to remove any dissolved carbon dioxide.

Titrate the germanium with a 0.02 *M* sodium hydroxide solution, standardized by titration of pure germanium metal dissolved in the same manner as the sample. Continue the titration past the first end-point (neutralization of strong acid), add a large excess of mannitol (*ca.* 10 g), and continue the titration to a second end-point. The volume of titrant required between the first and second end-points is used to calculate the amount of germanium in the sample.

Results and discussion

Amberlite XE-243 was first synthesized by Lyman and Preuss[4] by aminating a chloromethylated styrene–divinylbenzene copolymer with N-methylglucamine for use as a boron-specific ion-exchange resin. The boron specificity was based on the reaction between boric acid and the N-methylglucamine group, a polyhydric alcohol. A well-known analytical reaction of boric acid with a polyhydric alcohol is that of boric acid with mannitol, resulting in a stronger acid which can be titrated with sodium hydroxide. Several investigators[5,6] have characterized Amberlite XE-243 with respect to its interactions with boron, and others[7,8] have used the resin in the separation and determination of boron. No study as to the actual boron specificity of the XE-243 resin was available. Since the chemistry of germanium with respect to reactions with polyhydric alcohols is very similar to that of boron, the applicability of XE-243 to germanium chemistry is not surprising.

Although this work was not intended to provide a comprehensive characterization of an ion-exchange resin, an effort was made to determine the resin capacity and the column breakthrough capacity for the system being used. Table I contains some data obtained by batch equilibration methods in 1 *M* sodium hydroxide solutions. The amounts of germanium indicated were shaken with 1 g of XE-243 resin in 50 ml of 1 *M* sodium hydroxide for 4 h. An aliquot was removed and the germanium remaining in solution was determined by the germanium–mannitol titration; the amount of germanium on the resin was determined by difference. The batch experiments were done with: (*a*) the resin as received, (*b*) resin which had been pretreated by equilibration with both 3 *M* hydrochloric acid and 3 *M* ammonia solution, as described previously, and air-dried, (*c*) resin pretreated as described in (*b*), and then vacuum-dried at room temperature for 18 h. From the data in Table I, it is apparent that the resin capacity is an

TABLE I

GERMANIUM CAPACITY OF AMBERLITE XE-243 IN 1 *M* SODIUM HYDROXIDE

Resin pretreatment	*mg Ge in 50 ml 1 M NaOH*	*mmole Ge retained per 1 g resin*
As received	78.4	0.139
Acid–base–air dry	136.5	0.170
	73.7	0.143
	53.2	0.121
Acid–base–vacuum dry	91.5	0.520
	63.8	0.286
	51.5	0.226

equilibrium property, *i.e.*, the greater the ion concentration in solution, the greater the quantity retained by the resin. However, the data do indicate an approximate capacity of 0.1–0.2 mmoles of germanium per gram of resin for the conditions used in the analytical procedure. Similar experiments done in 0.1 *M* sodium hydroxide show that the capacity of the resin for germanium almost doubles. Also of interest is the indication that the pretreatment of the resin with strong acid and base solutions does not significantly change the capacity of the resin with respect to germanium.

The breakthrough capacity of the columns used in this work was determined by passing a 1 *M* sodium hydroxide solution containing 1 mg ml^{-1} of germanium through the column and checking the effluent for germanium by atomic absorption techniques. For the 30 × 1 cm (i.d.) columns at a flow rate of 2 ml min^{-1}, the breakthrough capacity was found to be 75 mg of germanium.

The accuracy of the method is limited by the germanium–mannitol titration and the manipulation of the sample. The ion-exchange separation of germanium and silicon has been shown to be quantitative by atomic absorption techniques for qualitative analyses of the effluents. The percentage recovery of germanium from the column, for pure germanium standards, was found to be $100 \pm 0.3\%$ which is the same order of recovery obtained by fusing germanium in sodium hydroxide and titrating the sample directly. Typical results obtained on a sample of SiGe alloy with a nominal germanium content of 59% (by weight) were $58.86 \pm 0.09\%$ with a maximum spread of 0.27% for three determinations. Interferences in the systems of interest, Si–Ge–P and Si–Ge–B, are limited to boron which is retained on the ion-exchange column and eluted with the germanium. The nominal boron content of the Si–Ge–B system is *ca.* 0.1%; the interference caused is within the experimental error of the germanium determination and, in most instances, would be ignored. In work demanding highest possible accuracy or involving samples containing higher boron contents, the boron may be determined as described on p. 481 and the germanium results adjusted appropriately.

SILICON

The gravimetric determination of silicon by dehydration of silica with perchloric acid and subsequent volatilization of the silicon with hydrofluoric acid is a time-honored analytical method[9]. However, the application of this classical method to silicon–germanium alloy is not mentioned in the literature. A variation of the method, which eliminates any possible interference by germanium, is reported here.

Experimental

Procedure. Samples in either powder or chunk form may be used in this analysis. However, powder allows the fusion step to be completed more rapidly. A sample is taken which will yield *ca.* 0.2 g of silica.

Weigh the prepared sample into a Zircaloy crucible and add *ca.* 10 g of sodium hydroxide pellets. Cover the crucible with a nickel or other suitable cover and fuse as described in the procedure for germanium. Cool the melt and dissolve in distilled water. The final volume of the solution, following washing, is *ca.* 200 ml.

Add 100 ml of concentrated hydrochloric acid (A.R.) carefully to the solution, and boil to remove the germanium as the chloride. When the solution is reduced in volume to *ca.* 200 ml, add 70 ml of 70% perchloric acid and evaporate to strong fumes.

(Caution: The final strong heating of the acid must be done in a special perchloric hood and care taken to avoid spattering of the salts.)

After cooling, dissolve the salts in distilled water. Filter the dehydrated silica, fire in a weighed platinum crucible, cool, and reweigh to obtain the weight of silica plus impurities. Then volatilize the silica by adding X ml of 48% hydrofluoric acid plus 3 drops of concentrated sulfuric acid to the crucible, and evaporating to dryness. Fire the crucible, cool and reweigh. The differential weight is the weight of the SiO_2.

Results and discussion

Standards, as such, for Si–Ge alloy are nonexistent. However, alloys made to have identical concentrations of silicon were analyzed by the above method, and the results indicated that the errors in duplicate analysis were far less than the reproducibility of the manufacturing process.

A series of duplicate analyses were run on 14 samples of Si–Ge alloys formulated to contain *ca.* 61 wt.-% silicon. The results indicated the alloy can be produced within a limit of 60.89±0.52 wt.-% silicon. However, the maximum deviation of duplicate analyses was only ±0.18 and the mean deviation for the duplicate runs was ±0.10.

The classical perchloric acid method for silicon is generally accepted to be more accurate than is indicated by the analytical results shown above. The limiting factor in the accuracy of SiGe analyses is probably inhomogeneity within a particular sample. Detailed studies of homogeneity, by this modified procedure, showed widely variable compositions in slices taken from a single zone leveled rod or from a single hot-pressed piece.

PHOSPHORUS

After a brief literature survey relative to the determination of phosphorus used as a dopant in semiconductor and thermoelectric materials, it was apparent that most investigators (*e.g.* O'Connor[10]) had used neutron activation techniques. Polarographic[11] and spectrophotometric methods based on molybdenum blue[12] are described for materials such as $CdSiP_2$ and $CdGeP_2$ which contain phosphorus as a major constituent. In attempting to adapt these techniques to the SiGe system, problems such as time required for analysis and the chemical behavior of the SiGe alloys became apparent, and a different approach was sought.

Here, a spectrophotometric method for the determination of phosphorus based on the reaction of molybdate with a solution containing vanadate and phosphate, first reported by Misson[13], is proposed for use in determining phosphorus dopant levels in SiGe alloys. Commonly described as the molybdovanadophosphate method, the method has been applied to phosphorus determination in materials such as fertilizers[14], iron ore and plain carbon steels[15], copper-base alloys[16], and titanium and zirconium and their alloys[17]. The method herein is basically a procedure described by Elwell and Wood[17] for determination of phosphorus in titanium alloys which has been modified for use in SiGe systems. It has been shown to be rapid and of sufficient accuracy for phosphorus dopant levels ranging from 0.01 to 0.55% by weight in a SiGe matrix.

Experimental

Reagents. All reagents and chemicals used in this work were of A.R. quality and were used with no further purification.

Apparatus. Absorbance measurements were made in 5-cm Beckman Near Infrared Silica cells with a Beckman DK-2A Ratio Recording Spectrophotometer using a tungsten or deuterium source and a photomultiplier detection system.

Preparation of blank and standard curve. Add 12 ml of (1 + 1) sulfuric acid to a 250-ml volumetric flask and dilute to *ca.* 100 ml. Add 3 ml of aqueous 0.5% (w/v) potassium permanganate solution, followed by sufficient aqueous 0.3% (w/v) sodium nitrite solution to reduce the permanganate. Add 10 ml of 10% (w/v) ammonium tartrate solution and dilute the solution to 250 ml. To 100 ml of this solution (pipetted) add 5 ml of 0.25% ammonium vanadate solution in 2% nitric acid, followed by 5 ml of an aqueous 20% (w/v) solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. Allow to stand for 15 min and then use as the blank for the absorbance measurements.

Obtain the standard phosphorus curve from solutions prepared in an identical manner with the exception of the addition of known amounts of phosphorus. Add the phosphorus as a standard solution of potassium dihydrogen phosphate before the addition of permanganate. Measure the absorbances of these solutions relative to the blank solution at 400 nm in 5-cm cells and a color development time of 15 min.

Treatment of sample. Use sufficient sample to provide 0.2–0.4 mg of phosphorus. Dissolve the sample in a 70-ml platinum dish by addition of *ca.* 4 ml of (1 + 1) nitric acid, followed by a dropwise addition of 48% hydrofluoric acid until dissolution is complete. Add 2 ml of 48% hydrofluoric acid in excess, followed by 12 ml of (1 + 1) sulfuric acid and evaporate to fumes of sulfur trioxide. Add 5 ml of water and transfer the solution to a beaker with 20 ml of (1 + 1) hydrochloric acid. Evaporate to fumes of sulfur trioxide, cool, dilute with 25 ml of water and heat to boiling. Add *ca.* 3 ml of aqueous 0.5% (w/v) potassium permanganate and boil for 1–2 min; add sodium nitrite solution dropwise until the pink color disappears. Transfer the solutions to 250-ml volumetric flasks containing 100 ml of water and 10 ml of the above ammonium tartrate solution and dilute to volume. Pipette 100-ml aliquots into plastic beakers, and add 5 ml each of the above-mentioned vanadate and molybdate solutions. After 15 min, measure the absorbance at 400 nm *vs.* a blank prepared at the same time as the unknown solutions. Establish the amount of phosphorus from the standard phosphorus curve.

Results and discussion

In a study of possible interference in the molybdovanadophosphate method, Kitson and Mellon[15] found that small amounts of silicate do not interfere. In the present work, it was shown that germanium causes high results for phosphorus. The removal of the silicon–germanium matrix by distillation of the tetrafluoride and tetrachloride as described in the Sample Treatment section was shown to be quantitative in the case of germanium; however, trace amounts of silicon remained in solution, probably because of a slight attack on the glassware used after the distillation of silicon tetrafluoride.

The color development time of 15 min was suggested by Elwell and Wood[17] and is consistent with minimum time of analysis. In this work, a decrease in percent transmittance (T) of the solution with time was observed. Solutions in the range of 40–

50% T showed a decrease of *ca.* 2.2% T over the period 15–75 min after color development. On a standard phosphorus curve prepared by making measurements 15 min after color development, the change corresponded to an increase of 0.015 mg phosphorus. At this rate of change, the change occurring during the absorbance measurements of a series of four solutions is negligible.

The phosphorus blank resulting from reagents and glassware was determined by carrying a blank determination through the entire procedure and measuring the absorbance of the resulting solution *vs.* a blank solution prepared as described above. The phosphorus blank was found to be 0.01–0.02 mg of phosphorus.

The accuracy of the method as applied to SiGe alloys is somewhat difficult to determine since true standards are not available. Secondary standards can be prepared by addition of known amounts of phosphate to undoped SiGe alloys, or by addition of phosphate to mixtures of silicon and germanium oxides. This can only approximate the actual matrix as SiGe alloys contain phosphorus in the elemental form.

Independent analyses done by neutron activation yielded a value of 0.42% on a sample which, by the proposed method, was found to contain 0.49%. The data in Table II show the accuracy obtainable on standards prepared by addition of known amounts of potassium dihydrogen phosphate to undoped SiGe alloys, the precision obtainable using the method, and the accuracy of the method relative to the nominal phosphorus content of the material being analyzed. In the range 0.2–0.5% phosphorus, the general spread in the data obtained by multiple analyses was 0.01% or less. The percent recovery for phosphorus added as phosphate to undoped SiGe alloy was 100±5% within the range 0.1–0.3 mg of phosphorus.

TABLE II

PHOSPHORUS CONTENTS *vs.* ANALYTICAL RESULTS ON SiGe ALLOYS

Sample	*Nominal P*	*P added as phosphate (mg)*	*P found (mg)*
Si–Ge	0.00	0.100	0.101
Si–Ge	0.00	0.200	0.207
Si–Ge	0.00	0.300	0.307
Si–Ge–P	0.50	—	0.480±0.004[a]
Si–Ge–P	0.30	—	0.314±0.011[a]
Si–Ge–P	0.52	—	0.508±0.006[a]

[a] Average of 5 determinations.

BORON

There are many spectrochemical methods for the determination of boron in a variety of matrices. The analysis of steel for boron has been well documented[18–20]. Boron has been determined in silicon by d.c. arc excitation[21]. Zil'bershtein[22] concentrated boron from high-purity silicon dioxide with hydrofluoric acid, and retained the boron with mannitol for a.c. arc analysis of the dried residue on graphite electrodes. The boron content of carbon and graphite has been reported by Feldman and Ellenburg[23] who used a d.c. arc with carbon electrodes or a sifter electrode system with high-voltage spark excitation. A.S.T.M. emission methods for the determination of boron in 14 different matrices are available[18]. However, there are no reports on the application of this technique to silicon–germanium alloys. Methods which fill this need are presented here.

Interest was divided between two levels of boron doping which demanded somewhat different spectrographic techniques. Therefore, two analytical methods, one of which is a solution technique applicable to doping levels between 0.1 and 0.2 wt.-% boron, and the other, a powder technique, applicable to lower boron concentrations, were developed.

No spectrographic standards for the SiGeB system were available and, because most quantitative spectrochemical methods are based on standards, it was necessary to use a method where synthetic standards could provide reliable analytical results for boron.

A solution procedure with a carbon rotating disk electrode was chosen for highly doped material because: (*a*) this laboratory has extensively used rotating disk solution procedures for many matrices; (*b*) synthetic standards could be prepared in a suitable concentration range; (*c*) an added internal standard could be used since neither silicon nor germanium would be at a constant percentage; (*d*) the inherent higher precision of the high-voltage spark source should result in a better overall method. For the lower doping levels, it was apparent that the sensitivity of the rotating disk spark procedure was inadequate, hence effort was directed towards a powder technique which used an ignited a.c. arc for excitation. It was considered impractical to make synthetic standards for the powder method by mixing powders of silicon, germanium and boron; therefore, a boron-doped SiGe alloy characterized by the solution method, was "diluted" by additions of n-type (boron-free) SiGe semiconductor material to produce powders with a range of boron contents. Carbon was added to these standards to make them electrically conductive.

Experimental

Apparatus and reagents. The spectrograph used for both of these boron methods was a 3.4-m Ebert with a grating of 15,000 lines/inch. Electrodes were National Carbon: L4072 (ASTM D-2) rotating disk and L4006 cupped lower electrode. The photographic plates were Eastman Kodak III-0 for the solution procedure and SA # 1 for the powder method. D-19 Developer was used in processing. Carbon for the powder method was obtained from the Ultra Carbon Corporation (UCP2-100). A Jarrell-Ash Model 23-100 Microphotometer was used for obtaining line transmittances.

All chemicals used were of A. R. grade or better.

Rotating disk solution spark procedure. A high-voltage spark discharge is produced between a carbon counter electrode and a 0.5-in. diameter rotating carbon disk electrode (Rotating Disk Assembly with tantalum shaft, rotating at 10 rev min^{-1}) which dips into a solution of the sample. Fresh solution is continuously brought into the analytical gap by rotation of the disk. Record the spectra photographically. Obtain transmittances for the boron line, adjacent background, and the nickel internal standard line for both standards and samples.

Standard and sample preparation (*solution method*). Weigh high-purity silicon and germanium and place in plastic beakers (Table III). Add 10 ml of 1 *M* citric acid,

TABLE III

COMPOSITION OF SOLUTION STANDARDS FOR BORON ANALYSES

Standard number	*Si (g)*	*% Si*	*Ge (g)*	*% Ge*	*B (0.001 g ml^{-1}) (ml)*	*% B*
GS-1	0.07805	78.01	0.0218	21.79	2.0	0.20
GS-2	0.07195	71.95	0.0277	27.7	3.5	0.35
GS-3	0.06505	65.05	0.3435	34.35	6.0	0.60
GS-4	0.06205	62.17	0.3695	37.02	8.0	0.80
GS-5	0.06995	69.88	0.03005	30.02	1.0	0.10

2 ml of concentrated nitric acid and 1 ml of 48% hydrofluoric acid. Place a tight fitting plastic lid on each beaker and heat the contents over a steam bath[2]. Add more nitric and hydrofluoric acid as required to dissolve the silicon and germanium standards. Add an aliquot of a standardized boric acid solution to each beaker (see Table III), and transfer the sample to a 100-ml plastic volumetric flask for final volume adjustment. Dissolve 0.1-g samples of the SiGe alloys using the same procedure.

Transfer 20 ml of each standard or sample to 1-oz dropping bottles to which 1 ml of nickel internal standard solution (0.05 g Ni ml^{-1}) was added. (Nickel was chosen as an internal standard since it was not a normal impurity in this material, and a nickel line was within 10.0 nm of the boron line of interest.) Record the spectra in triplicate for each standard and sample using the conditions summarized in Table IV. Use the

TABLE IV

INSTRUMENT PARAMETERS—EMISSION SPECTROSCOPY

(Spectrograph 3.4-m Ebert, 15,000 1/in. (2nd order); slit width, 40 μm; spectral range (2nd order), 210.0–335.0 nm; filter 2-step, percent transmission, 100/12)

	HV spark	*Ignited a.c. arc*
Capacitance, μF	0.0075	0.005
Inductance, μHz	155	625
Resistance, ohms	0	0
Voltage, primary, V	220	220
Breaks per half cycle	6	7
Power setting, spark	6	6
Power setting, arc	—	6
RF current, A	7	17.5
Electrode, upper	6″ × ¼″[a]	L3955
lower	ASTM D2	L4006
Preburn, s[b]	8	21
Exposure, s[b]	58	38
Emulsion type	III-0	SA #1
Developer D-19, min[c]	4	4
Stop bath (acetic acid), s	20	20
Fix, Kod Rapid, min	2	2

[a] National Carbon Rod, SPK L3828, rounded end.
[b] Controlled by stopwatch.
[c] Nitrogen burst, 3 s on, 10 s off.

two-step iron method for emulsion calibration with a preliminary curve[18,24]. Obtain the transmittances of the boron 249.678-nm line[25], adjacent background, and the nickel 259.590-nm line and determine the background-corrected boron-to-nickel relative intensity ratios from the emulsion calibration curve. Plot these ratios against boron concentration on log–log graph paper to produce the analytical curve. Obtain the boron concentrations for the unknown samples by applying the ratios to the analytical curve.

Ignited a.c. arc powder method. A spark-ignited 110-V a.c. arc is used to excite powdered standards and samples packed in the lower cupped graphite electrode countered with a rounded end graphite electrode. Spectra of standards and samples are obtained on photographic plates. Transmittances of the boron line, adjacent background, and the aluminum internal standard line are used in establishing the analytical curve.

Standard and sample preparation (powder method). Use two SiGe powders (200 mesh), one boron-free, the other containing 0.14% boron, to prepare standards. Mix each powder with 9 parts of carbon (containing 1% alumina for use as an internal standard). Mixtures of these two base powders result in a set of standards for boron in the matrix of interest (Table V). Powder solid samples by crushing in a Plattner mortar and pestle, sieve through 200-mesh nylon screen, and mix 1 part of sample to 9 parts of carbon (containing 1% alumina). All mixing was done in 2-in. high, 0.5-in. diameter lucite vials with a 0.375-in. diameter lucite ball. Mixing time was 2 min in a Wig-L-Bug. Pack the electrodes by pressing the cupped portion of the electrode into the powder. Use graphite with a rounded end as the counter electrode. Record spectra of standards and samples in triplicate, following the conditions outlined in Table IV. Calibrate the emulsion as outlined for the rotating disk. Obtain transmittances of the boron 249.678-nm line, adjacent background, and the aluminum 256.799-nm line for subsequent conversion to corrected relative intensity ratio of boron to aluminum. Conversion of relative intensity ratios to boron concentration is similar to that outlined above.

TABLE V

COMPOSITION OF POWDERED STANDARDS FOR BORON ANALYSES

Standard no.	*Boron base (parts)*	*Boron-free base (parts)*	*% B*
B1400	1	0	0.14
B930	2	1	0.093
B700	1	1	0.070
B460	1	2	0.046
B280	1	4	0.028
B140	1	9	0.014
B70	1	19	0.007
B28	1	49	0.0028
B Base	0	1	0.000

Results and discussion

Table VI compares the intended concentration of boron and the results by both methods. From this comparison and the percentage differences, it may be concluded that the rotating disk spark procedure yields results within ±5% in the range 0.1–0.8%. For the ignited a.c. arc powder method, the reproducibility is *ca.* ±10% in the

TABLE VI

BORON CONTENTS *vs.* ANALYTICAL RESULTS ON SiGe ALLOYS

Sample	*Analyzed wt.-%*	*Intended concentration wt.-%*	*% deviation*
Ignited a.c. arc method			
6P	0.0031	0.00298	+4
7P	0.0063	0.00595	+5.9
8P	0.026	0.0238	+9.2
9P	0.061	0.0595	+2.5
Rotating disk spark method			
2A3	0.125	0.12	+4.2
SP1	0.14	0.15[a]	+7.0
SP2	0.146	0.15[a]	+2.6

[a] Produced by "spiking" SiGe material.

range 0.002–0.09 %. The accuracy of the methods could not be evaluated owing to the lack of primary standards.

The solution spectrochemical procedure yielded adequate precision and sensitivity for boron in the range 0.1–0.8 % (by weight). The solution standards were made to contain varying amounts of silicon and germanium which served two purposes: to determine if the boron response was influenced by the matrix, and to make possible simultaneous analyses for silicon and germanium, if desired. When the boron concentration was lowered, it was necessary to use a higher sensitivity source to retain reasonable precision. A moving plate study was made to compare the ignited a.c. arc burnout of aluminum and boron with time. The relative intensity ratio of boron to aluminum was essentially constant from 20 s to 60 s; therefore, a 20-s preburn was chosen. Aluminum was substituted for nickel for internal standardization in the more sensitive method because boron and aluminum have evaporation rates more similar than those of nickel and boron (this is not significant in solution analysis).

SUMMARY

The performance of thermoelectric devices is sensitive to the chemical composition, the dopant concentration and the uniformity of the semiconductor materials used in their fabrication. Analytical methods for the determination of silicon, germanium, boron, and phosphorus in SiGe thermoelectric materials are described. These methods were developed because of the fragmentary data available in the literature regarding their chemical characterization. The methods are rapid, accurate, and, with the exception of boron, require a minimum of expensive apparatus. Germanium was determined acidimetrically by means of the mannitol complex after ion-exchange separation on Amberlite XE-243, silica by the conventional gravimetric method, phosphorus colorimetrically as the vanadomolybdophosphate, and boron by emission spectroscopy.

RÉSUMÉ

On décrit des méthodes d'analyse pour le dosage du silicium, du germanium, du bore et du phosphore dans le matériel thermoélectrique SiGe. Elles sont rapides, précises; et, à l'exception du bore, elles ne nécessitent pas un appareillage coûteux. Le germanium est dosé acidimétriquement, en présence de mannitol, après séparation sur Amberlite XE-243; la silice par méthode gravimétrique conventionnelle; le phosphore colorimétriquement comme vanado-molybdophosphate et le bore par spectroscopie d'émission.

ZUSAMMENFASSUNG

Die Leistungsfähigkeit thermoelektrischer Bauelemente hängt von der chemischen Zusammensetzung, der Dotierungskonzentration und der Gleichförmigkeit des Halbleitermaterials ab, dass bei der Herstellung verwendet wird. Analytische Methoden für die Bestimmung von Silicium, Germanium, Bor und Phosphor in thermoelektrischen SiGe-Materialien werden beschrieben. Diese Methoden wurden wegen der unvollständigen Angaben entwickelt, die in der Literatur bezüglich der chemischen Charakterisierung zu finden sind. Die Methoden sind schnell, genau und erfordern, von Bor abgesehen, ein Minimum kostspieliger Apparaturen. Germanium wurde mit Hilfe der Mannitkomplexe nach Ionenaustausch-Abtrennung an Amberlite XE-243 acidimetrisch bestimmt, Siliciumdioxid nach der herkömmlichen gravimetrischen Methode, Phosphor kolorimetrisch als Vanadatomolybdatophosphat und Bor durch Emissionsspektroskopie.

REFERENCES

1 F. D. Rossi, Thermoelectricity and Thermoelectric Power Generation, *Solid State Electronics*, Vol. 11, Pergamon Press, 1968, pp. 833–868.
2 K. L. Cheng and B. L. Goydish, *Anal. Chem.*, 35 (9) (1963) 1273.
3 H. J. Cluley, *Analyst*, 76 (1951) 517.
4 W. Lyman and A. Preuss, *U.S. Pat.* 2, 813, 838, Nov. 19, 1957.
5 R. Kunin and A. F. Preuss, *Ind. Eng. Chem. Prod. Res. Develop.*, 3 (1964) 304.
6 F. Pinon, J. Deson and R. Rosset, *Bull. Soc. Chim. Fr.*, 8 (1968) 3454.
7 R. M. Carlson and J. L. Paul, *Anal. Chem.*, 40 (1968) 1292.
8 R. M. Carlson and J. L. Paul, *Soil Sci.*, 188 (4) (1969) 266.
9 H. Furman, *Standard Methods of Chemical Analysis*, Vol. 1, 6th Ed., 1962, p. 955.
10 J. O'Connor, *Sci. Tech. Aerosp. Rep.*, 2 (6) (1964) 737.
11 R. Yu. Lyalikova, *Zavod. Lab.*, 55 (4) (1969) 431.
12 R. Yu. Lyalikova, *Zh. Anal. Khim.*, 23 (81) (1968) 1240.
13 G. Misson, *Chem. Ztg.*, 32 (1908) 633.
14 W. C. Hanson, *J. Sci. Food Agr.*, 1 (1950) 172.
15 R. E. Kitson and M. G. Mellon, *Ind. Eng. Chem. Anal. Ed.*, 16 (1944) 379.
16 W. T. Elwell and H. N. Wilson, *Analyst*, 81 (1956) 136.
17 W. T. Elwell and D. F. Wood, *The Analysis of Titanium, Zirconium and Their Alloys*, Wiley, 1961.
18 ASTM, *Methods for Emission Spectrochemical Analysis*, 6th Ed., 1971, pp. 40–163.
19 C. R. Hines and J. K. Hurwitz, *Appl. Spectrosc.*, 21 (1967) 277.
20 J. Goryczka and W. Klimecki, *Pr. Inst. Hutn.*, 18 (1966) 45.
21 A. N. Shteinberg, *Tr. Inst. Met. Akad. Nauk SSSR*, 11 (1962) 229.
22 K. I. Zil'bershtein, O. N. Nikitina and M. P. Semov, *Poluch. Anal. Veshchestv Osoboi Chist. Mater. Vses. Konf., Gorky, USSR*, 1963, pp. 139–141.
23 C. Feldman and J. Y. Ellenburg, *Anal. Chem.*, 27 (1955) 1914.
24 J. R. Churchill, *Ind. Anal. Chem.*, 16 (1944) 653.
25 *MIT Wavelength Tables*, The M.I.T. Press, 1969.

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SHORT COMMUNICATION

Mixed ligand complexes formed with copper(II)-1,10-phenanthroline complex and some bidentate ligands

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Copper(II) reacts with 1,10-phenanthroline (Phen) and bengal red, the latter of which has no chelate-forming ability, to form an intensely colored ternary complex. The reaction has been used for the spectrophotometric determination of copper[1]. Recently, Sone *et al.*[2] have studied, from a structural viewpoint, the absorption spectra of some mixed copper(II) chelates containing Phen (or 2,2'-bipyridine) and a bidentate ligand, but no analytical application has been made. It would be expected that the replacement of the bengal red by a chelate-forming organic dye would also lead to the formation of a mixed ligand complex suitable for the spectrophotometric determination of copper. In the present communication is described a spectrophotometric study of the reactions between the 1:1 copper–1,10-phenanthroline complex, Cu(Phen), and four bidentate ligands, pyrocatechol violet (PV), alizarin red S (ARS), eriochrome cyanine R (ECR) and chromazurol S (CAS). The applicability of the above reactions to the spectrophotometric determination of traces of copper is also discussed.

Experimental

All the reagent solutions used were prepared from reagent-grade chemicals or from purified ones. Hexamethylenetetramine–hydrochloric acid buffer solution was used for pH adjustment. A small amount of gum arabic solution was used as a dispersing agent in order to prevent precipitation of the mixed ligand complexes.

Absorbance curves were recorded with a Model 124 Hitachi spectrophotometer with 1.0-cm quartz cells. A Toa Dempa HM-6A type pH meter was used for pH determinations. All the measurements were made at 25 ± 0.1°.

Results and discussion

The visible absorption spectra of the mixed ligand complexes were taken under the optimal conditions, the spectral data being given in Table I.

For the Cu–Phen–pyrocathecol violet and Cu–Phen–alizarin red S mixed ligand complexes, in which pyrocatechol violet or alizarin red S may be bonded to copper through two phenolic hydroxyl groups, a large bathochromic shift in the position of the absorption maximum was observed along with a large hyperchromic effect. It appears that this can be understood by assuming a double bonding character between the oxygen atom in the coordinating pyrocatechol violet or alizarin red S

TABLE I

PROPERTIES OF THE MIXED LIGAND COMPLEXES
($\mu=0.1$, KCl)

Complex	*Absorption maximum* (*nm*)	*Molar absorptivity* ($l\ mol^{-1}\ cm^{-1}$)	*Formation constant* ($K^{Cu(Phen)}_{Cu(Phen)L}$)
Cu–Phen–PV	703	$4.0\cdot10^{4}$	$5.0_0\cdot10^{14}$
Cu–Phen–ARS	560, 595	$9.4\cdot10^{3}$[a]	$2.8_8\cdot10^{12}$
Cu–Phen–ECR	550	$2.5\cdot10^{4}$	$3.1_4\cdot10^{13}$
Cu–Phen–CAS	580	$2.1\cdot10^{4}$	$3.6_1\cdot10^{14}$

[a] At 595 nm.

and the central copper, which would make the π–π^* transition of the ligand dye much easier than that in the corresponding binary complex. It should be noted here that two maxima were observed in the visible absorption spectrum of the Cu–Phen–alizarin red S mixed ligand complex, whereas only one maximum was observed in that of the copper–alizarin red S binary complex. The spectrum of the mixed ligand complex strongly resembles that of the fully deprotonated alizarin red S, suggesting that copper is bonded to two phenolic oxygen atoms of the alizarin, releasing two protons.

On the other hand, for the Cu–Phen–eriochrome cyanine R and Cu–Phen–chromazurol S mixed ligand complexes, in which the second ligand may be bonded to copper through one phenolic hydroxyl group and one carboxyl group, a slight hypsochromic shift was observed along with a small hyperchromic effect. This may be explained as being due to the electron-withdrawing behavior of the carboxyl group in the coordinating eriochrome cyanine R or chromazurol S, since there will be no remarkable interligand steric hindrance in these mixed ligand complexes.

The combining ratios of copper, Phen and ligand dyes in the mixed ligand complexes were determined at pH 6.9 by the mole ratio and the continuous variation methods. Both methods clearly showed the formation of 1:1:1 mixed ligand complexes.

The formation constants of the mixed ligand complexes, $K^{Cu(Phen)}_{Cu(Phen)L}$, were then evaluated spectrophotometrically at an ionic strength of 0.10, with solutions containing Cu(Phen) and the ligand dyes in equimolar concentrations, $2.0\cdot10^{-5}\ M$. The pH values of the solutions were varied in the range where the dissociation and hydrolysis of Cu(Phen) do not occur in any appreciable extent. The values for the acid dissociation constants of the ligand dyes were taken from previous investigations[3-6]. The formation constants thus obtained are also listed in Table I. These values indicate that the reactions are applicable to the spectrophotometric determination of copper when $2\cdot10^{-5}\ M$ reagent solutions are used and the pH values of the solutions are adjusted respectively to $\geqslant 6.7$, $\geqslant 7.3$, $\geqslant 7.0$ and $\geqslant 6.0$ for the PV–, ARS–, ECR– and CAS–mixed ligand complexes. In fact, up to about 1.3 p.p.m. of copper can be successfully determined at pH 6–9 with sufficient amounts of chromazurol S and a small excess of Phen. The color development occurs instantaneously. The method is very sensitive and thus suitable for the spectrophotometric determination of traces of copper. Larger amounts of Phen, however, interfere with the copper determination probably by forming $Cu(Phen)_2$. It was also found that an addition of nickel(II) or zinc(II) effectively prevented formation of $Cu(Phen)_2$ when the copper determination is carried out with pyrocatechol violet in the presence of excess of 1,10-phenanthroline. Further details on the determination of copper with 1,10-phenanthroline and these organic dyes will be reported elsewhere.

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REFERENCES

1 B. W. Baily, R. M. Dagnall and T. S. West, *Talanta*, 13 (1966) 753; 13 (1966) 1661.
2 K. Sone, S. Utsuno and T. Ogura, *J. Inorg. Nucl. Chem.*, 31 (1969) 117.
3 O. Ryba, J. Cifka, M. Malat and V. Suk, *Colle t. Czech. Chem. Commun.*, 21 (1956) 349.
4 M. Otomo and K. Tonosaki, *Talanta*, 18 (1971) 438.
5 V. Suk and V. Miketukova, *Collect. Czech. Chem. Commun.*, 24 (1959) 3629.
6 F. J. Langmyhr and K. S. Klausen, *Anal. Chim. Acta*, 29 (1963) 149.

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ANNOUNCEMENT

The A. A. Benedetti-Pichler Award Committee of the American Microchemical Society is pleased to announce that the recipient of the 1972 Award is Professor Lyman C. Craig of The Rockefeller University in recognition of his outstanding contribution to microchemistry. Among the many outstanding accomplishments of Dr. Craig is the universal acceptance of the Craig countercurrent distribution system for the separation and purification of organic molecules existing in a complicated mixture. The award, in the form of a bronze plaque, will be presented at the Eastern Analytical Symposium at Atlantic City on November 1, 1972, after an address by the recipient.

Dr. Craig was with the Rockefeller Institute for many years before joining the faculty of the Rockefeller University. He has published over 150 papers, dealing with alkaloids, antibiotics, hormones, peptides, proteins, heterocyclic compounds, medicinals, dialysis and trace analysis, in analytical, biological and chemical journals.

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