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## ON THE PREPARATION OF ION-SELECTIVE ELECTRODES

*Four types of ion-selective electrodes were designed and tested for  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$  and  $\text{UO}_2^{2+}$  in the range  $10^{-1}$  —  $10^{-6}$  M. Pressed pellet membranes based on silver sulfide were used for the  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ion sensors. Copper sulfide-silver sulfide, a silver dithiolate-silver salt, and  $\text{UO}_2[\text{TCNQ}]_2$  were used as electroactive materials in plastified graphite electrodes. For  $\text{UO}_2^{2+}$  electrodes a liquid membrane was also tested.*

### 1 — INTRODUCTION

One of the most significant advances in analytical chemistry in recent years has been the development of ion-sensors, particularly the solid-state and liquid-membrane ion-selective electrodes.

Those devices, capable of measuring ion activities, can also be used to determine total free ion concentrations through methods such as titration and ionic strength buffering. Measurements are rapid (the response time being of order of  $10^{-2}$ s to 2 minutes) nondestructive, easy and requiring simple equipment.

The possibility of making electrodes of any size and shape and the increasing number of species that can be detected has made this tool of great interest in fields such as biochemistry, geological prospecting, oceanography and water pollution.

The main limitations concern accuracy, particularly over long periods and uncertainty associated with the definition of ion activity.

Easy construction and the idea that an ion-selective electrode can be made for almost any ionic species encouraged us to look for the possibilities of developing our own devices using old and new materials and try to develop a  $\text{UO}_2^{2+}$  ion sensor which would be of great interest in the nuclear field.

### 2 — THE IDEAL NERNST ELECTRODE

The crucial part of an ion selective electrode is a sensing membrane which allows only the ion of interest to pass from the sample solution at the outer membrane surface to an internal solution in contact with the inner membrane surface. This solution contains an activity of the ion, which is not significantly affected by the negligible amount of ions that cross the membrane and is therefore considered constant.

It works on the basis that changes in the membrane potential develop, when placed in the sample solution. This is due to a momentary flux of ions across the membrane, in the direction of the solution containing the lower activity of the mobile ion. The final potential is established when equilibrium is attained preventing further net movement of ions.

These changes in the membrane potential can be measured with a high impedance voltmeter or poten-

tiometer connected across an appropriate reference electrode, in contact with the inner solution, and an external reference electrode in contact with the sample solution through a salt bridge.

The measured potential is given by the Nernst equation

$$E = E_0 + \frac{2.3 RT}{zF} \log A \quad (1)$$

where  $E$  is the potential in millivolts. The constant  $E_0$  depends on the particular choice of reference electrodes used, on the ion activity of the inner solution and on the liquid junction.  $RT/F$  is the Nernst factor which multiplied by 2.3 gives 59.16 mV at 25 °C.  $z$  is the charge of the ion and  $A$  the sample solution activity of the ion to which the membrane is permeable.

In a medium of constant ionic strength the actual value of the activity coefficient needs not be known, since it is constant throughout the various experiments and can be included in  $E_0$ , when calibrations are made.

### 3 — LIQUID MEMBRANE AND SOLID-STATE ELECTRODES

In a liquid membrane electrode, ion exchange can take place between the sample solution and an ion-site in an organic phase insoluble in water. The site group must be capable of going into rapid ion exchange equilibrium with the ion of interest. Selectivity requires that the ion-site forms a more stable complex with the ion to be detected than with any potentially interfering ion in the sample solution.

The empirical equation [1]

$$E = E_0 + \frac{2.3 RT}{z_A F} \log \left[ A + \sum_i K_i B_i^{z_B/z_A} \right] \quad (2)$$

is usually considered. In this equation,  $K_i$  are selectivity constants,  $A$  and  $B_i$  being the activities of the sought-for ion and interfering ions, respectively. In order to have a good selectivity the term containing the interfering ion activities must be negligible compared to  $A$ .

In the solid state devices, the electroactive material which constitutes the membrane has to be a good ionic conductor, chemically inert in the sample solution and of low solubility.

Solid state membranes are usually very selective due to the restriction to the movement of all ions except the one to be detected. Conduction is due to a lattice defect mechanism in which a mobile ion adjacent to a vacancy moves into it, this being the right size and shape. All other ions are unable to move and cannot contribute to the process.

Silver sulfide being a low resistance ionic conductor in which the silver ions are the mobile species is an ideal electroactive material. In fact it has a very low solubility product, an excellent chemical resistance and it is easily shaped into pressed pellets with good mechanical properties.

By itself, it can be used to detect silver according to the Nernst equation or to measure sulfide activities in agreement with the equation

$$E = E_0' - \frac{2.3 RT}{2F} \log A_{S^{2-}} \quad (3)$$

where

$$E_0' = E_0 + \frac{2.3 RT}{2F} \log K_{sp} \quad (4)$$

which is obtained from the Nernst equation introducing the solubility product.

It can also be used as a matrix material for other metal sulfides, to make membranes sensitive to the corresponding metal ion. The concentration of silver sulfide in the matrix has to provide good silver ion conducting pathways.

In solutions containing no silver ions the mixed membranes have a Nernstian behaviour determined by the two solubility products

$$(A_{Ag^+})^2 \cdot A_{S^{2-}} = K_{sp(Ag_2S)} \quad (5)$$

$$A_{M^{2+}} \cdot A_{S^{2-}} = K_{sp(MS)} \quad (6)$$

from which

$$A_{Ag^+} = \left[ \frac{K_{sp(Ag_2S)}}{K_{sp(MS)}} M^{2+} \right]^{1/2} \quad (7)$$

to be introduced into the Nernst equation giving

$$E = E_0' + \frac{2.3 RT}{2F} \log A_{M^{2+}} \quad (8)$$

The solubility product of the metal sulfide must be much larger than the solubility product of silver sulfide in order to have  $Ag_2S$  present at the electroactive surface, but it has to be sufficiently small for the metal ion activity in the sample solution due to the solubility of MS to be negligible, relative to the level expected in the sample.

Liquid and solid state membranes can be used in conjunction with materials, such as graphite, which do not take any part in establishing the measured potential, merely acting as inert electron donors or acceptors.

Liquid membranes can be impregnated into graphite electrodes giving very resistant and reliable devices. Graphite can be hydrophobised with water insoluble organic liquids, teflon or other polymers and the solid electroactive material can be deposited on the graphite surface or incorporated in a graphite body, making a large variety of ion-sensors.

## 4 — EXPERIMENTAL

### 4.1 — APPARATUS

The ion selective electrodes described in this study were used in connection with Radiometer potentiometers type PHM 4d.

Commercial saturated calomel electrodes (Radiometer and Beckmann) were used as reference electrodes except with silver nitrate test solutions in which case we preferred silver-silver chloride electrodes [2] in a  $AgNO_3$  0.1M/ $KNO_3$  1M solution connected to the test solution via a salt bridge.

This arrangement was shown to give similar results but better response times for the silver ion electrodes, when compared to other arrangements, namely the calomel reference and silver/silver chloride/sodium or potassium chloride systems.

A commercial Select-Ion Beckmann 39 612- $Cu^{2+}$  electrode was used for comparison purposes.

All measurements were carried out in vessels thermostated at 25 °C with Cora ultra-thermostats type KLZ 42.60-2-160D.

### 4.2 — REAGENTS

Chemicals of analytical grade (Merck and BDH) were used without further purification.

Series of standard solutions were prepared by suitable dilution of stock solutions, keeping the ionic strength at 0.1 M by addition of appropriate volumes of 1 M potassium nitrate solution. All solutions were prepared from water which had been both deionized and distilled. Stock solutions were kept in polyethylene bottles and the silver nitrate ones were protected against light. Titrations vs. EDTA performed to assure the correct titres.

### 4.3 — PREPARATION OF MEMBRANE RAW MATERIALS

The metal sulfides were prepared by two methods:

- i) Precipitation by bubbling hydrogen sulfide through an aqueous solution of lead, silver or copper (II) nitrate to precipitate  $PbS$ ,  $Ag_2S$  or  $CuS$  respectively, in a way similar to that described as precipitate IV in reference 3.
- ii) By a direct method [4] involving the reaction of the appropriate metal powder with sulfur to produce the metal sulfide. The reaction takes place in a furnace at 500 °C and in an atmosphere of hydrogen sulfide. The lead and copper precipitates were obtained from a mixture in a molar ratio 1:1 and the silver sulfide in a molar ratio 2:1.

A silver salt of the silver complex of maleonitriledithiolene with the formula  $Ag_2[Ag_2 S_4 C_4 (CN)_4]$  was used as a silver electroactive material. This complex salt was prepared in the dark and as described in reference 5. It was used on the basis of our knowledge of its high ionic conductivity and low solubility [6].

The  $UO_2^{2+}$  electroactive solid material based on tetracyanoquinodimethane (TCNQ) [7, 8] was prepared by adding an aqueous solution of  $LiTCNQ$  to an aqueous solution of  $UO_2(NO_3)_2$  in excess. The green solid, of formula  $UO_2[TCQN]_2$  was collected on a filter and dried in a vacuum desiccator.

The  $UO_2^{2+}$  liquid membrane was prepared as follows [9]: Alamine'336 (Tricaprylyl Tertiary Amine from Kankakee, Illinois) in petroleum ether 0.1 M

containing 3.5% isodecanol is added to a  $\text{UO}_2\text{SO}_4$  water solution with a concentration of  $1 \text{ gdm}^{-3}$  in  $\text{UO}_2^{2+}$  and a pH in the range 1-2.

The  $\text{UO}_2^{2+}$  saturated organic phase is obtained after successive extractions in a separating funnel (until the yellow colour remains in the aqueous phase).

#### 4.4 — PREPARATION OF ELECTRODES

Four types of ion-selective electrodes were prepared. The first one being of the silver sulfide pressed pellet type [4] and the other three using graphite as a support [3, 10, 11].

*Type A — Pressed pellet membranes based on silver sulfide:* Those electrodes were prepared from mixtures containing 70% silver sulfide and 30% copper or lead sulfide. The sulfides were grinded, and pellets, 13 mm in diameter and 1 mm thick, were obtained by pressing the powder in a press to about  $10 \text{ tons cm}^{-2}$ .

Those pellets were then mounted on teflon rods as shown in fig. 1a. The teflon rods were heated at about  $100^\circ\text{C}$  in an oven and the pellets introduced in the right place exerting a slight pressure. After cooling, the pellets were properly tight. The electrical contacts were made by a stainless steel rod pressing against a silver spot in the inside surface of the pellet with the aid of a spring. The silver spots were easily obtained by adding a small amount of silver powder to the sulfide mixture previously inserted in the dye as the pellets were pressed.

*Type B — Plastified graphite:* In those electrodes, fig. 1b, the electroactive materials were deposited on plastified graphite rods. These rods were prepared as follows: graphite rods with the final shape (13 mm diameter and 25 mm long) were degassed overnight in a vacuum chamber and then immersed in a monomer mixture (36% acrylonitrile, 54% styrene and 10% carbon tetrachloride). Those rods were then carefully wrapped in aluminum foil and packed in plastic bags, to prevent evaporation of the monomer mixture, and placed in the chamber of a 10 000 Curie gamma irradiator for 8 hours. Radiation polymerizes the monomer mixture leaving the graphite pores filled with polymer and therefore preventing the penetration of solution

into the body of the electrode. Those rods were then mounted on teflon stems as described for the pellets, the stainless steel rod was screwed into the graphite body and the electroactive material was rubbed into the surface and polished.

In the case of the  $\text{Cu}^{2+}$  electrode the electroactive material used was a mixture of silver sulfide and copper sulfide (70%, 30%). For the electrodes based on silver/silver-maleonitriledithiolate the electroactive material was the salt itself properly grinded and dried.

*Type C — Pressed graphite-teflon tablets:* The  $\text{UO}_2^{2+}$  electrodes were prepared by pressing a mixture of graphite-teflon powder and  $\text{UO}_2[\text{TCNQ}]_2$ . The copper electrodes were prepared by rubbing the silver sulfide-copper sulfide mixture over the compressed graphite-teflon pellet.

*Type D — Liquid membrane:* The liquid membrane,  $\text{UO}_2^{2+}$  electrodes were prepared by impregnating graphite rods, fig. 1b, with the alamine- $\text{UO}_2^{2+}$  complex in the way described for the plastification of graphite.

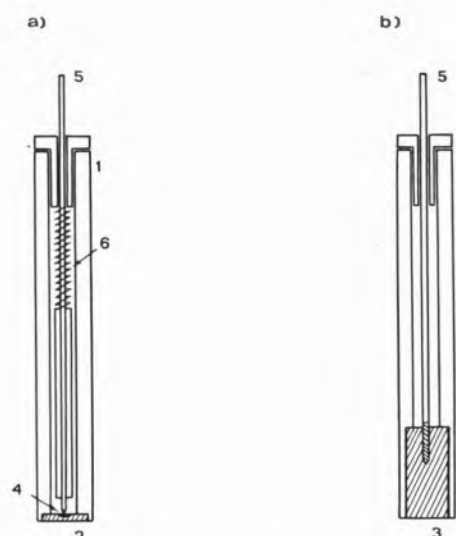


Fig. 1

*Ion-selective electrodes:* a) pressed pellet type; b) plastified graphite or liquid membrane type. 1 — teflon body; 2 — pellet; 3 — graphite rod; 4 — silver spot; 5 — stainless steel rod; 6 — spring

While not in use, the electrodes were generally stored in distilled water, but similar results were obtained for electrodes kept in air. For the  $\text{UO}_2^{2+}$



type D electrodes, however, the results reported in this paper were obtained for devices stored in the alamine- $\text{UO}_2^{2+}$  saturated organic solution and then placed in distilled water for 15 minutes before use.

## 5 — RESULTS

Electrodes of the various types were tested in magnetically stirred standard solutions over the range  $10^{-1} - 10^{-6}$  M in the particular metal ion, at constant ionic strength of 0.1 M.

The measured potentials were plotted on potential vs. pM ( $-\log [M^{z+}]$ ) graphs according to equation

$$E = E_0' - \frac{59.16}{z} \text{ pM} \quad (9)$$

Saturated calomel electrodes were used as reference except for the silver ion-sensors, for which an  $\text{AgCl}/\text{Ag}$  electrode was used.

Detailed results are given below.

### 5.1 — COPPER (II) ELECTRODES

Series of copper (II) electrodes of types A, B and C were tested giving good characteristics, in general with response times of a few seconds. Potential vs. pCu plots are shown in fig. 2 and slopes and  $E_0'$  values are listed on Table 1 for some of the devices tested.

All electrodes display nernstian behaviour over the  $10^{-1} - 10^{-5}$  M range with slopes from  $-29.30$  mV to  $-26.74$  mV, close to the theoretical value of

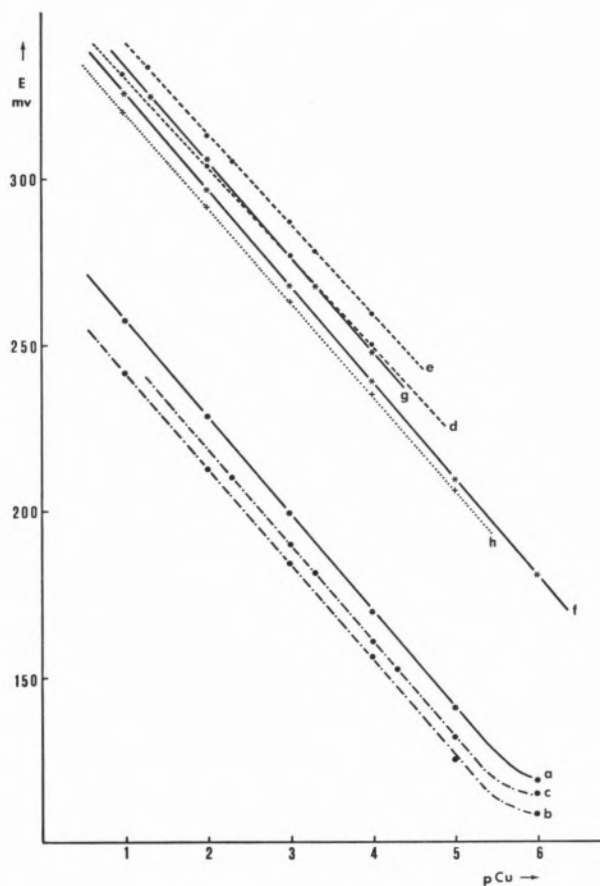


Fig. 2

Potential vs. pCu plots for the Cu(II) electrodes: a) Cu A 1; b) Cu A 4; c) Cu A 4, five months later; d) Cu B 2; e) Cu B 2, five months later; f) Cu B 3; g) Cu B 3, five months later; h) Cu C 6

$-29.60$  mV. Tests made five months apart show that, in general, the slope is maintained within less than 0.5 mV but  $E_0'$  values drift up to 10 mV in some cases, demonstrating the need of periodic calibration.

Table 1

Copper(II) electrodes

	Cu A 1	Cu A 4		Cu B 3		Cu B 2		Cu C 6
		initial	5 months later	initial	5 months later	initial	5 months later	
slope	$-29.30$	$-28.87$	$-28.97$	$-29.07$	$-28.67$	$-26.74$	$-27.10$	$-28.41$
$E_0'$	287.28	270.47	276.66	354.99	362.67	357.30	367.30	348.41

The loss of nernstian response below  $10^{-5}$  M was a characteristic of most electrodes at least for non-buffered solutions, which should not indeed be used as standards below this range [12].

$E_0'$  values for types B and C are close, what could be expected since the electrical contacts are graphite-stainless steel in both cases.

The selectivity of these electrodes was tested in solutions containing different metal ion species such as Ni(II) and Pb(II) at various concentrations. No interferences were detected except in the presence of  $\text{Cl}^-$  and acetate ion, certainly due to precipitation of silver chloride or complexation, respectively, at the membrane surface.

## 5.2 — LEAD(II) ELECTRODES

Only type A lead(II) electrodes were tested and some results are displayed on fig. 3 and Table 2.

Table 2

Lead (II) electrodes

	Pb A 2	Pb A 6
slope	— 28.00	— 25.51
$E_0'$	96.20	94.40

Response times are longer than for the copper(II) electrodes but still within the range of a few seconds. Response is still nernstian but with a slope lower than the theoretical one. Similar selectivity tests indicate that ion species such as Ni(II) and Cu(II) do not interfere but interferences due to  $\text{Cl}^-$  and acetate are still more pronounced than for the copper(II) electrodes.

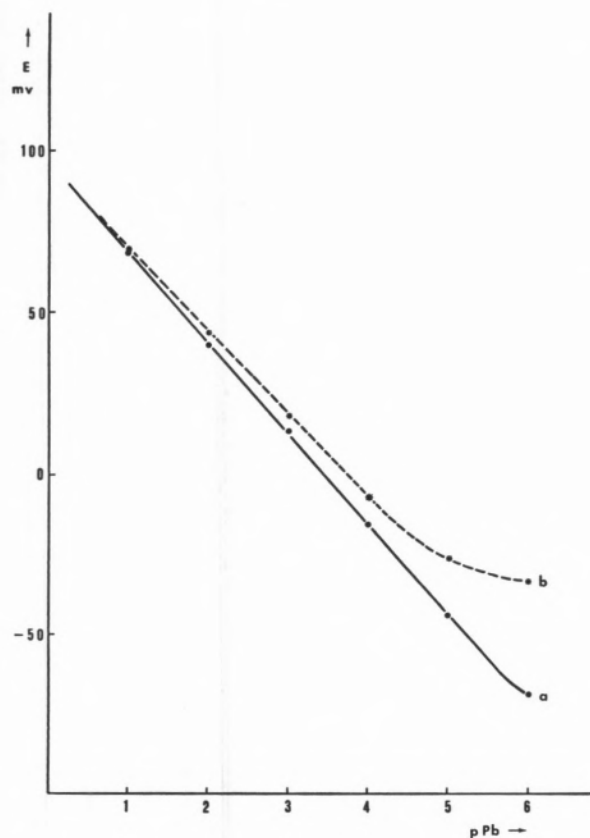


Fig. 3

Potential vs.  $p\text{Pb}$  plots for the Pb(II) electrodes: a) Pb A 2; b) Pb A 6

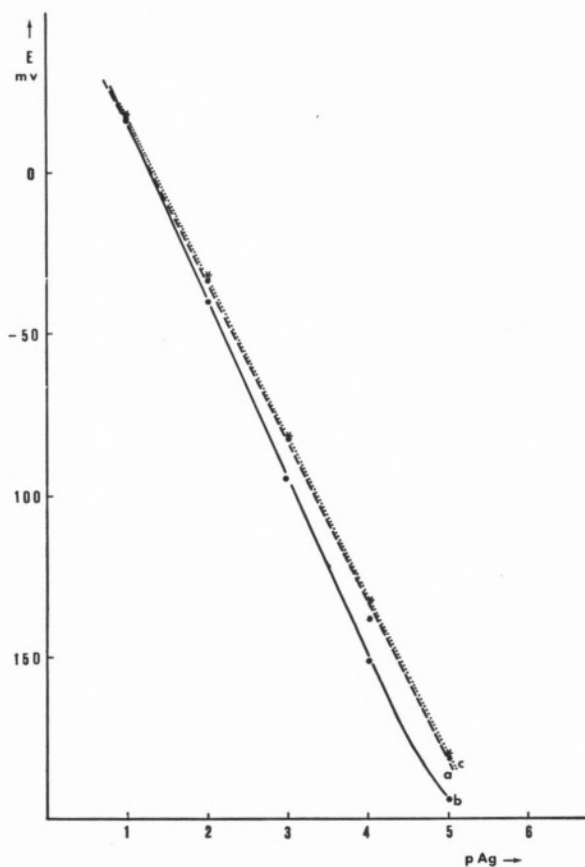


Fig. 4

Potential vs.  $p\text{Ag}$  plots for the Ag electrodes: a) Ag B 1; b) Ag B 2; c) Ag B 3.

## 5.3 — SILVER ELECTRODES

The silver-ion selective electrodes based on the silver-maleonitriledithiolate silver salt are in general very reproducible and stable but slopes range from  $\approx -50$  to  $-55$  mV, therefore lower than nernstian ( $-59.16$  mV). Results obtained with a AgCl/Ag reference electrode are shown in fig. 4 and Table 3. No interferences were detected for cationic species but they were found for chloride, iodide and sulfide ions. This high cationic selectivity is certainly due to the stability of the silver complex and its very low solubility product.

## 5.4 — URANYL ELECTRODES

Two types of uranyl ion-sensors were tested. The type C,  $\text{UO}_2^{2+}$  electrodes, based on  $\text{UO}_2$  [TCNQ] $_2$  have very good reproducibility and good nernstian

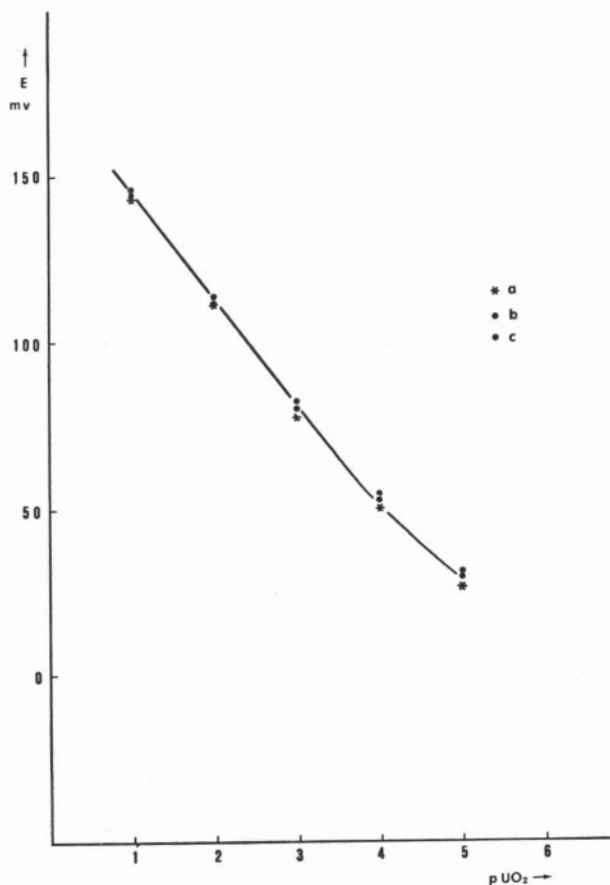


Fig. 5

Potential vs.  $p\text{UO}_2$  plots for electrodes: a)  $\text{UO}_2$  C 15; b)  $\text{UO}_2$  C 16; c)  $\text{UO}_2$  C 17

Table 3

Silver electrodes

	Ag B 1	Ag B 2	Ag B 3
slope	-49.88	-53.27	-49.70
$E_0'$	65.76	64.85	66.50

behaviour. About twenty electrodes of this type were tested with similar results. Fig. 5 shows the behaviour of three of them, which display almost superimposed data, Table 4.

A dozen of liquid membrane, type D electrodes was tested as well. The alamine- $\text{UO}_2^{2+}$  liquid membrane was either incorporated on graphite-teflon compressed pellets as in electrode  $\text{UO}_2\text{D}5$  or supported on graphite rods as in electrodes

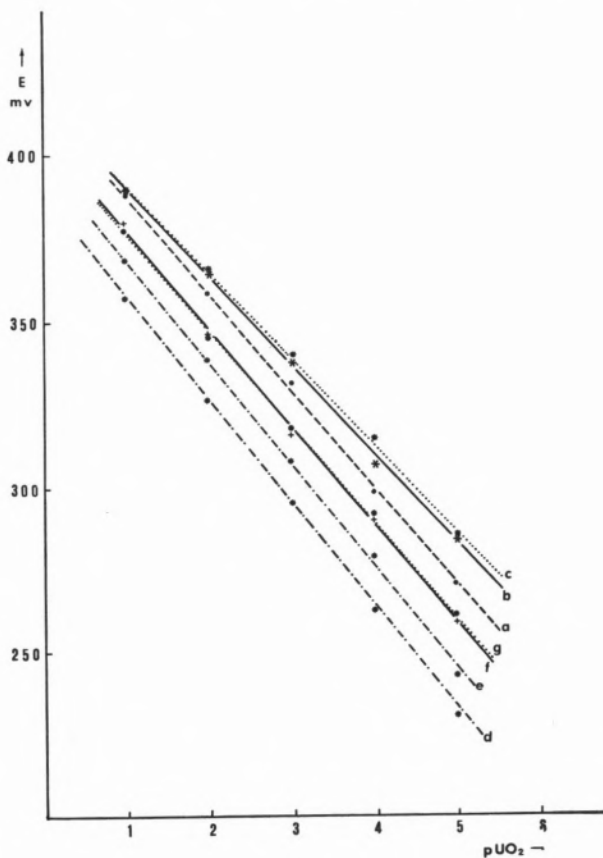


Fig. 6

Potential vs.  $p\text{UO}_2$  plots for electrodes: a)  $\text{UO}_2$  D 5; b)  $\text{UO}_2$  D 6; c)  $\text{UO}_2$  D 6, six days later; d)  $\text{UO}_2$  D 7; e)  $\text{UO}_2$  D 7, six days later; f)  $\text{UO}_2$  D 10; g)  $\text{UO}_2$  D 10, six days later

Table 4

Uranyl electrodes, type C

	UO <sub>2</sub> C 15	UO <sub>2</sub> C 16	UO <sub>2</sub> C 17
slope	— 33.27	— 30.59	— 30.31
E <sub>0</sub> '	180.35	173.78	173.70

UO<sub>2</sub>D6, 7 and 10. Fig. 6 shows the behaviour of electrodes of this type. Results obtained on freshly prepared electrodes and on the same electrodes six days later, show that they keep linear response and slope but in some cases a drift in the E<sub>0</sub>' value is observed. Table 5 displays the obtained values of slopes and E<sub>0</sub>' for the above mentioned electrodes.

Both types of electrodes deteriorate rapidly and therefore can only be used with confidence after recent calibration with solutions containing the same ionic species as the unknowns to avoid interferences which seem to be common in these cases. We did not attempt a detailed study on selectivity but our preliminary experiments indicate that some problems are to be expected.

Response times were less than one minute for concentrations above 10<sup>-3</sup> M increasing to about three minutes as concentrations were lowered to 10<sup>-6</sup> M.

## 6 — CONCLUSION

Ion-selective electrodes based on insoluble, stable and good ionic conductors at room temperature, such as silver sulfide or the silver-dithiolate salt are normally very reliable.

There is not, as yet, a complete understanding of the processes involved, particularly those occurring at the membrane surface, but the state of the art enables us to say that electrodes based on such materials can easily be made without much cost in any moderately equipped laboratory.

The fact that no particular internal reference is needed in the devices described, can easily be explained by assuming that the electrical contact between the internal membrane surface and the silver spot in the case of the electrodes based on silver sulfide acts as an internal solid state reference electrode.

As for graphite electrodes we still have a constant activity of the particular ion in the vicinity of the stainless steel electrical contact. For this contact to behave as an internal reference, we have to assume however, that the free electrons of the conducting graphite play a role in the process.

Thinking of the importance of conducting electrons in electrode processes, TCNQ salts would be ideal materials since they are electronic semiconductors with the possibility of easy ionic exchange and complexes of almost any cation can be made. Unfortunately they are not insoluble enough, what limits the range of linear response.

A promising possibility is to insolubilize these materials by incorporation in inert polymer matrices. Organic semiconductors and semiconducting polymers are undoubtedly a field to explore since a large variety of inorganic and organic positive and negative ions can be combined in those systems. Our results on the uranyl ion-sensors, although not yet of great interest to the analytical chemist, are undoubtedly promising as a starting point in the search for a reliable electroactive material to be used in an ion-sensitive device for UO<sub>2</sub><sup>2+</sup>.

Table 5

Uranyl electrodes, type D

	UO <sub>2</sub> D 5	UO <sub>2</sub> D 6		UO <sub>2</sub> D 7		UO <sub>2</sub> D 10	
		initial	6 days later	initial	6 days later	initial	6 days later
slope	— 29.70	— 26.27	— 26.83	— 31.83	— 31.38	— 29.88	— 28.65
E <sub>0</sub> '	418.50	417.81	417.15	389.55	401.54	407.64	404.63



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## RESUMO

Construíram-se e ensaiaram-se quatro tipos de eléctrodos selectivos para  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$  e  $\text{UO}_2^{2+}$  na gama de  $10^{-1}$  —  $10^{-6}$  M. Para os eléctrodos de  $\text{Cu}^{2+}$  e  $\text{Pb}^{2+}$  usaram-se membranas de pastilha baseadas em sulfureto de prata. Como materiais electro-activos em eléctrodos de grafite plastificada usaram-se misturas de sulfureto de cobre-sulfureto de prata, um sal de prata, de um ditiolato de  $\text{UO}_2[\text{TCNQ}]$ . Para o ião  $\text{UO}_2^{2+}$  também foi testada uma membrana líquida.