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Cd (II)-selective potentiometric sensor with multilayer solid membrane based on selenide and its applications

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The present paper has set itself to develop and characterize a new selenide-based cadmium-sensitive multilayered solid membrane material, with a view to optimizing its composition and improving its electrodic qualities. It has also set itself to achieve a cadmium-selective sensor with the help of this membrane and to determine its functional characteristics. For this, the influence of various factors is studied upon the electrodic function of the sensor, with consequences in the enlargement of the Nernstian response range and implicitly, in lowering the detection limit. Also, the selectivity coefficients are determined by means of the two methods, of separate solutions and of mixed-up solutions, an addition being made to the method of separate solutions, which allows the rapid determination of the selectivity constant. The performance of the proposed sensor is compared to that of the "classical" cadmium sulphide-based electrode and this proving higher qualities particularly regarding the detection limit and selectivity. The electrode was tested on galvanic water and it exhibit suitable characteristics for routine analysis of cadmium in real samples.

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1. Introduction

While some heavy metals such as copper, iron, manganese, zinc, cobalt, nickel, vanadium, molybdenum, and even chrome and lead, in small quantities, are indispensible to the good functioning of the human body, cadmium is toxic in any concentration.

Cadmium may reach the human body through the polluted air or drinking water or through contaminated foodstuffs, and it accumulates, especially in kidneys, liver and muscles, causing a series of severe affections of the renal tract, the gastro-intestinal tract, the reproductive tract, of the bone system, the central nervous system, the immune system, due to the blocking of same chemical processes taking place at cellular level. It has cumulative effects in the body, such that, at higher concentrations and on long exposure, it can destroy the DNA and develop cancer.

Because the concentration of cadmium in the air, water or foodstuffs is low and, also, because the quantity in which it is harmful to the human body is low, developing of extremely sensitive analysis methods as well as of sensors having a detection limit as low as possible is needed.

There are many procedures for determining cadmium in various specimens, of which atomic absorption spectroscopy, cold vapor atomic absorption spectroscopy, flam atomic absorption spectroscopy - electrothermal atomization, anodic stripping voltammetry, chromatography, gravimetric detection are most frequently used. However, these methods, although exact and accurate, are, on the one hand, laborious, due to the pre-treatment that must be applied to samples and, on the other hand, they require pretentious materials. For these reasons, they cannot be used in carrying out a large number of analyses.

Potentiometry, direct or by titration, is a simple procedure which does not require a laborious preparation of the samples; it is fast and, therefore, proper for serial determinations. Although a large number of Cd-selective sensors, with both solid [1-2] and liquid [3-14] membrane have been studied, researches have shown that only a small number of them have proved highly effective, regarding the detection limit, cadmium selectivity in the presence of other cations, the response time and the life span. Also, researches carried out so far have not fully solved the problem of he processes taking place in the optimization of membranous materials composition.

This is why we consider that the study on the composition of the membrane and on the performance of a new type of Cd-selective sensor, based on the selenide of this metal is welcome. It is exactly what the present paper sets itself to do, it attempting to determine the optimum composition and the electrodic qualities of a multilayered membrane consisting of CdSe-Ag_2S-Ag, as well as to determine the functional parameters of the Cd-sensitive sensor devised with this membrane.

Extension of the Nernstian response range was considered, with a view to lowering the detection limit and improving the response time, with a cadmium selectivity as high as possible, in the presence of other cations.

Compared with a “classical” sensor, based on sulphide, the selenide-based sensor has shown an extension of the Nernstian response range by a decade towards lower values of cadmium (II) concentration, while maintaining and even improving the performance regarding response time, selectivity and life span.

2. Experimental

2.1 Reagents. The checking solutions set

Cadmium selenide, used as the active component in the preparation of the membrane, was of Merck origin. The silver sulphide, used as matrix, was prepared in the laboratory by precipitation under heat, from a silver nitrate solution with sodium sulphide solution, in stoechiometric ratio. Precipitation was followed by aging, washing, filtrating and drying to constant weight of the precipitate [13].

The checking solutions were obtained from two stocks solutions of cadmim nitrate of $1\cdot10^{-1}$ M and $5\cdot10^{-2}$ M concentration, respectively, by successive dilutions with potassium nitrate 0.32 M concentration (for adjusting the ionic strength to the constant value J = 0.32). 11 standard solutions were obtained with concentrations ranging between $1\cdot10^{-6}$ - $1\cdot10^{-1}$ M Cd^{2+}. 15 mL of acetic buffer solution were added to each checking solution for adjusting pH to the value of 4.7.

2.2 Potential measurement cell. Apparatus

The following electrochemical cell was used:

Hg / Hg_2Cl_2 / saturated KCl / sample / membrane ($CdSe + Ag_2S$) / Ag / internal cable

The selenide-based sensor was used as measuring electrode and a saturated double-joint calomel electrode as a reference electrode.

The experiments were carried out at the surrounding medium temperature (20 ± 2°C) and the potential was measured by means of a pH-meter of Hanna Instruments, HI 8817 type.

2.3 Obtaining of the membrane. Devising of the sensor

The membranous material was obtained by mixing up the two components, active (CdSe) and matrix (Ag_2S), in various proportions, followed by grinding and mechanical shaking for homogenization. The CdSe and Ag_2S mixture was pressed in the shape of a tablet (5-8 mm in diameter) by means of a hand hydraulic press of Dezimal Presse DP-36 type, at 10^3 t/cm^2 [15]. Membranes of various compositions were prepared and investigated and those which showed best characteristics were selected for thorough study [16].

The sensors were manufactured in the some constructive variant as the sulphide-based ones, with three-layer membrane, CdSe + Ag_2S, Ag_2S, metallic Ag, with solid electric contact.

After manufacture, before utilization, the sensors were wet-ground on abrasive paper of various hardness and then polished on felt, wet and soaked in chrome trioxide.

3. Results and discussion

3.1 Determination of the optimum composition of the membranous material

To determine the optimum ratio of the two components of the membranous mixture, the following variants were studied:

a. *10 % CdSe + 90 % Ag_2S;*

b. *30 % CdSe + 70 % Ag_2S;*

c. *50 % CdSe + 50 % Ag_2S.*

The measurements were carried out on three consecutive days, the results being expressed as the mean across three successive daily determinations. Between measurings, the sensors were maintained in a dry conditions.

The determinations rescaled that for all three sensors, the electrodic function is linear within the concentration range of $5\cdot10^{-6}$ - $5\cdot10^{-2}$ M Cd^{2+}. The mean ratio mV/pCd is shown in Table 1 as a slope of the electrodic function. It can be noticed that the sensitivity of the sensors increases along the three days of measuring, and the sensor having the best behaviour, with the mV/pCd ratio closest to the Nernstian value, 29.1 at 20°C, is the ***b*** sensor. So, the optimum composition of the membranous mixture is 30 % CdSe + 70 % Ag_2S.

3.2 Influence of the thermal treatment upon the performance of the membranous material

For obtaining more sensitive membranes, the influence of the thermal treatment, at 235°C, in nitrogen atmosphere, upon the membranous mixture, before and after its being pressed as tablets, was studied. It is to be noted that, following application of the thermal treatment, the volume of the sintered material decreased while its color changed from black to grey-ashen which denotes structural changes.

The fact must be noted that, both before and after tablet formation, the thermal treatment applied to the membranous material leads to a diminution of the linear measurement range to values between $5\cdot10^{-5}$ - $1\cdot10^{-1}$ M Cd^{2+}, to the detriment of detection of low cadmium concentrations. The results obtained during two consecutive days of experimental measurings, expressed as the mean of three successive passages through the checking solutions, are presented in Tables 2a and 2b. A decrease in the sensitivity of the sensors is also to be noticed, expressed by mV/pCd ratio below 23.10, both in the case of application of the thermal treatment before and after pressing. By contrast to what literature says, namely that better results are obtained after thermal treatment of the membranous material, the study performed by us has proved that membranes not treated thermally have higher performance [16].

Table 1. The electrodic function of the three sensors during the three days of measurements.

Sensor	Membrane composition	Electrode function		
		First day	Second day	Third day
a	10 % CdSe + 90 % Ag_2S	E = 33.6 - 20.1 pCd	E = 34.0 - 21.9 pCd	E = 40.5 - 25.4 pCd
b	30 % CdSe + 70 % Ag_2S	E = 36.4 - 23.0 pCd	E = 37.8 - 27.8 pCd	E = 43.0 - 29.1 pCd
c	50 % CdSe + 50 % Ag_2S	E = -28.8 - 19.5 pCd	E = -24.9 - 22.0 pCd	E = -29.2 - 22.2 pCd

Table 2a. The electrodic function of the three sensors over two days of determinations, with thermal treatment applied to the membrane before pressing.

Sensor	Membrane composition	Electrode function	
		First day	Second day
a	10 % CdSe + 90 % Ag_2S	-	-
b	30 % CdSe + 70 % Ag_2S	E = - 120.76 -18.99 pCd	E = - 112.69 -20.13 pCd
c	50 % CdSe + 50 % Ag_2S	E = - 79.38 -21.34 pCd	E = - 75.89 -22.82 pCd

Table 2b. The electrodic function of the three sensors over two days of determinations, with thermal treatment applied to the membrane after pressing.

Sensor	Membrane composition	Electrode function	
		First day	Second day
a	10 % CdSe + 90 % Ag_2S	E = - 97.62 -22.43 pCd	E = - 94.58 -23.10 pCd
b	30 % CdSe + 70 % Ag_2S	E = - 98.20 -20.88 pCd	E = -102.66 -19.43 pCd
c	50 % CdSe + 50 % Ag_2S	E = -178.92 -19.70 pCd	E = -174.89 -21.70 pCd

3.3 Influence of the conditioning of the sensor upon its performances

Further, the influence of the conditioning of the sensor in the reference solution, KNO_3 0.32 M and in the diluted solution, $1\cdot10^{-6}$ M Cd^{2+}, was studied, for 10 minutes, before each series of daily determinations. The measurings were performed also across three consecutive days, the results being expressed as the mean of three successive daily determinations and presented in Tables 3a and 3b under the form of the equations of the electrodic functions.

In the case of conditioning in the reference solution, the preservation of the linearity of the electrodic function over the range $5\cdot10^{-6}$ - $5\cdot10^{-2}$ M Cd^{2+} can be noticed, but an increase in the sensitivity of the sensors is also seen.

Considering that keeping the sensor in the reference electrolyte solution during measurements leads to a decrease in the ionic concentration of Cd^{2+} in the membrane, with impact on the exchange equilibrium and, implicitly, on the Nernstian response range and on the responding time, in the next phase, the reference solution was replaced by a $1\cdot10^{-6}$ M Cd^{2+} solution. Conditioning in the most diluted solution of the checking set leads to an extension of the linearity range towards great dilution, $1\cdot10^{-6}$ - $5\cdot10^{-2}$ M Cd^{2+}, concomitently with an increase in the mV/pCd ratio, so, in the sensitivity of the sensors. It should be noted that the sensor b, with the membrane composition 30 % CdSe + 70 % Ag_2S, preserves the best behaviour, its sensitivity coming close to the ideal value during the third day of determination (29.2 as against 29.1 at 20^{o}C).

Table 3a. The electrodic function of the three sensors conditioned in the reference solution.

Sensor	Membrane composition	Electrode function equation		
		First day	Second day	Third day
a	10 % CdSe + 90 % Ag_2S	E = 46.3 - 24.6 pCd	E = 45.0 - 24.2 pCd	E = 40.3 - 22.4 pCd
b	30 % CdSe + 70 % Ag_2S	E = 42.1 - 29.3 pCd	E = 43.2 - 29.5 pCd	E = 42.0 - 29.0 pCd
c	50 % CdSe + 50 % Ag_2S	E = - 32.6 - 22.1 pCd	E = - 21.5 - 28.0 pCd	E = - 24.9 - 27.0 pCd

Table 3b. The electrodic function of the sensors conditioned in the solution $1 \cdot 10^{-6}$ M Cd^{2+}.

Sensor	Membrane composition	Electrode function equation		
		First day	Second day	Third day
a	10 % CdSe + 90 % Ag_2S	E = 50.8 - 26.7 pCd	E = 50.1 - 26.2 pCd	E = 48.8 - 25.6 pCd
b	30 % CdSe + 70 % Ag_2S	E = 40.7 - 27.2 pCd	E = 44.9 - 28.9 pCd	E = 45.2 - 29.2 pCd
c	50 % CdSe + 50 % Ag_2S	E = - 22.1 - 27.1 pCd	E = - 22.6 - 27.2 pCd	E = - 23.1 - 26.8 pCd

Further, through testing was applied to the sensor with the optimum membrane composition. 4 sensors of the same type were used, with the membrane composition 30 % CdSe + 70 % Ag_2S, denoted by 1, 2, 3, 4. Before the measurements, the sensors were conditioned for 10 minutes in the solution $1 \cdot 10^{-6}$ M Cd^{2+}, and, between determinations, they were kept in a dry condition.

The Nernstian response range, the sensitivity of the sensors (the mV/pCd ratio), the reproducibility of the electrodic function of the four sensors, the reproducibility of the electrodic function of the same sensor over a short period of time, the reproducibility of the electrodic function of the same sensor over a long period, the response time, as well as the selectivity of the sensors to cadmium, in the presence of other cations, were studied.

3.4 Sensitivity of the sensor with the optimum membrane composition. Reproducibility of the electrodic function. Behaviour in time of the sensor

The measurements were also done across three consecutive days, three daily determinations for each of the four sensors. The electrodic functions of the sensor 1, on the first day of determinations, are shown in Fig. 1. The behaviour of the four sensors during the three days of determinations was similar. Table 4 shows the equations of the electrodic functions, over the three days of measurements, as means of daily determinations.

The linearity range for all the four sensors with optimum membrane composition is between $1 \cdot 10^{-6}$ - $1 \cdot 10^{-1}$ M Cd^{2+}. One can see in Table 4 the almost Nernstian behavior of the sensors, as well as the good reproducibility as regards the sensitivity and the correlation coefficient.

3.5 Sensitivity of the sensor with the optimum membrane composition. Reproducibility of the electrodic function. Behaviour in time of the sensor

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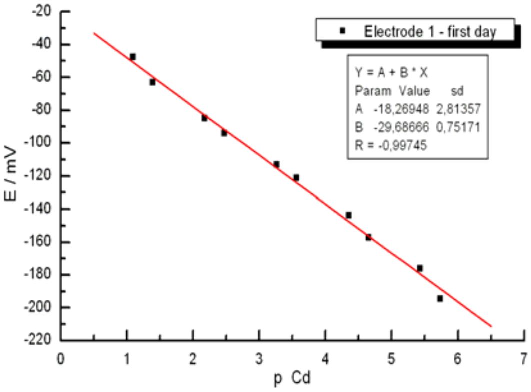

Fig. 1. The electrodic function of the sensor 1 during the first day of measurements (mean of daily determinations).

Fig. 2 shows the evolution of the sensitivity (the mV/pCd ratios) of the four sensors over the three days of determinations (mean of daily determinations).

Table 4. The equations of the calibration curves for the sensors with optimum membrane composition.

Sensor	First day		Second day		Third day	
	Electrode function	Corr. coeff.	Electrode function	Corr. coeff.	Electrode function	Corr. coeff.
1	EM = - (18.3 ± 2.8) - (29.7 ± 0.7) pCd	0.9974	EM = - (18.4 ± 2.35) - (29.2 ± 0.6) pCd	0.9982	EM = - (18.5 ± 1.9) - (28.7 ± 0.5) pCd	0.9988
2	EM = - (94.8 ± 2.9) - (29.9 ± 0.8) pCd	0.9973	EM = - (95.6 ± 2.43) - (29.2 ± 0.6) pCd	0.9980	EM = - (95.9 ± 2.2) - (28.7 ± 0.6) pCd	0.9984
3	EM = - (116.5 ± 2.2) - (29.9 ± 0.6) pCd	0.9984	EM = - (116.9 ± 1.95) - (29.2 ± 0.5) pCd	0.9987	EM = - (116.7 ± 1.7) - (28.7 ± 0.4) pCd	0.9990
4	EM = - (115.4 ± 2.4) - (29.7 ± 0.6) pCd	0.9981	EM = - (115.7 ± 2.33) - (29.3 ± 0.6) pCd	0.9987	EM = - (115.6 ± 1.9) - (28.8 ± 0.5) pCd	0.9987

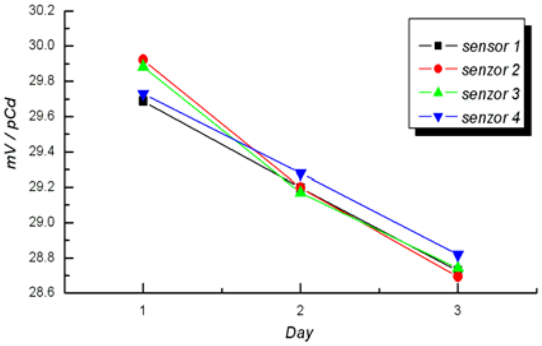

Fig. 2. The evolution of the slope of the electrodic function of the sensors with optimum membrane composition (mean of daily determinations).

Further, the behavior across time of the four sensors with optimum membrane composition was studied, the measurements being made over one month from their manufacturing. The results are shown in Table 5 and Fig. 3.

A slight depreciation of the sensitivity of the sensor can be noted, from mV/pCd = 29.7 to mV/pCd = 18.3, due to the oxidation of the membrane surface with oxygen from the air and from the determinations solutions. This is why, after this time interval, reconditioning of the membrane surface is recommended by grinding with abrasive paper, wet polish on the Cr_2O_3 or Na_2CO_3 imbued felt and immersion in 10^{-2} M Complexon III solution.

The behaviour of the sensors with optimum membrane composition over four weeks after reconditioning of the membrane surface by grinding is shown in Table 6 and Fig. 4.

Table 5. The equations of the calibration curves for the sensors over four weeks from the manufacturing.

Week / Day	Equations of calibration curves	Correlation coefficient
1 / 1	EM = - (18.3 ± 2.8) - (29.7± 0.7) pCd	r = 0.9975
1 / 2	EM = - (18.4 ± 2.3) - (29.2 ± 0.6) pCd	r = 0.9982
1 / 3	EM = - (18.5 ± 1.9) - (28.7 ± 0.5) pCd	r = 0.9988
2 / 1	EM = - (17.6 ± 2.8) - (28.1 ± 0.7) pCd	r = 0.9971
2 / 2	EM = - (16.7 ± 2.5) - (27.5 ± 0.7) pCd	r = 0.9976
2 / 3	EM = - (16.0 ± 2.4) - (27.0 ± 0.6) pCd	r = 0.9978
3 / 1	EM = - (5.4 ± 2.3) - (25.6 ± 0.6) pCd	r = 0.9977
3 / 2	EM = - (7.4 ± 2.0) - (24.6 ± 0.5) pCd	r = 0.9980
3 / 3	EM = - (9.7 ± 2.0) - (23.8 ± 0.5) pCd	r = 0.9980
4 / 1	EM = - (7.2 ± 1.8) - (22.9 ± 0.5) pCd	r = 0.9982
4 / 2	EM = - (7.4 ± 1.5) - (21.6 ± 0.4) pCd	r = 0.9987
4 / 3	EM = - (11.2 ± 1.7) - (20.3 ± 0.5) pCd	r = 0.9979
5 / 1	EM = - (5.5 ± 1.6) - (19.9 ± 0.4) pCd	r = 0.9981
5 / 2	EM = - (13.7 ± 1.5) - (18.5 ± 0.4) pCd	r = 0.9981
5 / 3	EM = - (12.2 ± 1.5) - (18.3 ± 0.4) pCd	r = 0.9981

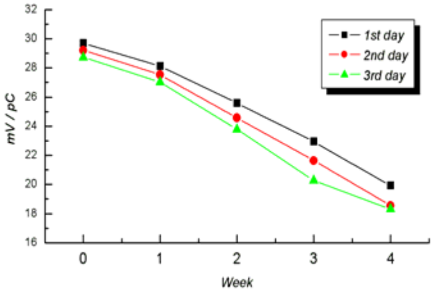

Fig. 3. The evolution of the slope of the electrodic function of the sensors over one month from their manufacturing (mean of daily measurements).

It is advisable that the electrodic function of the sensor be checked before utilization. If the functional parameters do not fall within the optimum values, the periodic reconditioning of the membrane surface by grinding and polishing is recommended. On the other hand, it is advisable to protect, as much as possible, the membrane surface against the attack of atmospheric agents when the sensor is being used.

The experiments carried out over a longer period of time of using Cd-sensitive sensors based on selenide prove that the periodic reconditioning of the surface keeps the sensor in a functioning condition for over a year. After that the in-depth degradation of the tablet - membrane makes the reconditioning by grinding no longer effective.

Table 6. The equations of the calibration curves for the sensors over four weeks from the reconditioning of the surface.

Week / Day	Equations of calibration curves	Correlation coefficient
1 / 1	EM = - (3.0 ± 2.0) - (29.6 ± 0.5) pCd	r = 0.9988
1 / 2	EM = - (3.5 ± 1.9) - (29.2 ± 0.5) pCd	r = 0.9988
1 / 3	EM = - (3.9 ± 2.0) - (28.9 ± 0.5) pCd	r = 0.9988
2 / 1	EM = - (16.1 ± 2.4) - (28.1 ± 0.6) pCd	r = 0.9980
2 / 2	EM = - (14.8 ± 2.1) - (27.3 ± 0.6) pCd	r = 0.9983
2 / 3	EM = - (16.5 ± 2.1) - (26.6 ± 0.6) pCd	r = 0.9981
3 / 1	EM = - (16.4 ± 1.4) - (26.6 ± 0.5) pCd	r = 0.9988
3 / 2	EM = - (17.8 ± 1.6) - (25.0 ± 0.4) pCd	r = 0.9989
3 / 3	EM = - (16.4 ± 1.8) - (24.7 ± 0.5) pCd	r = 0.9986
4 / 1	EM = - (12.8 ± 1.5) - (24.5 ± 0.4) pCd	r = 0.9989
4 / 2	EM = - (10.5 ± 1.3) - (24.3 ± 0.3) pCd	r = 0.9992
4 / 3	EM = - (13.2 ± 1.4) - (23.3 ± 0.4) pCd	r = 0.9990
5 / 1	EM = - (7.8 ± 1.3) - (22.8 ± 0.3) pCd	r = 0.9990
5 / 2	EM = - (10.5 ± 1.4) - (22.2 ± 0.4) pCd	r = 0.9989
5 / 3	EM = - (12.5 ± 1.4) - (21.9 ± 0.4) pCd	r = 0.9989

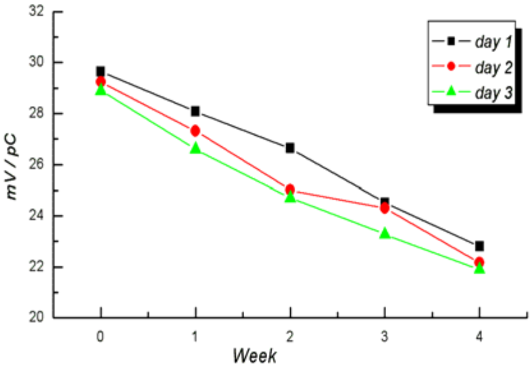

Fig. 4. Evolution of the slope of the electrodic function over one month from the reconditioning of the surface (mean of daily measurements).

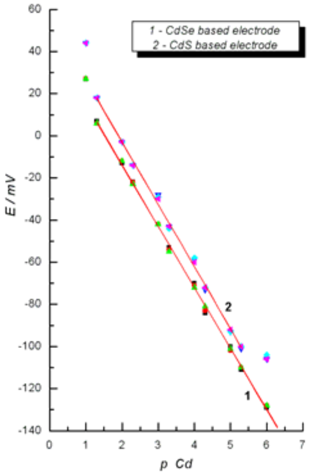

Fig. 5. Comparison between the electrode functions of a sensor based on selenide (1) and sulphide (2), respectively.

3.6 Comparison between the performance of Cd-ISME electrodes with selenide-based membrane and sulphide, respectively

In order to compare the electrode functions of the two sensors based on selenide (sensor 1) and sulphide (sensor 2), respectively, they were both conditioned, as shown above, by immersion, for 10 minutes before daily determinations, into the $1 \cdot 10^{-6}$ M Cd^{2+} solution. It is noted that the sensors with membrane based on selenide prove better characteristics than those with membrane based on sulphide, especially as regards the extension of the detection limit towards low values of the Cd^{2+} ion concentration in solution.

3.7 Response time

Fig. 6 shows the variation of the potential of sensor 1 on the first day of determinations, on the first passage through the 11 solutions of the checking set. It is noticed that, in the more concentrated solutions of $1 \cdot 10^{-3}$ M Cd^{2+}, the potential of the sensor stabilizes after one minute from immersion into solution, while in the more diluted solutions, the response time is two minutes.

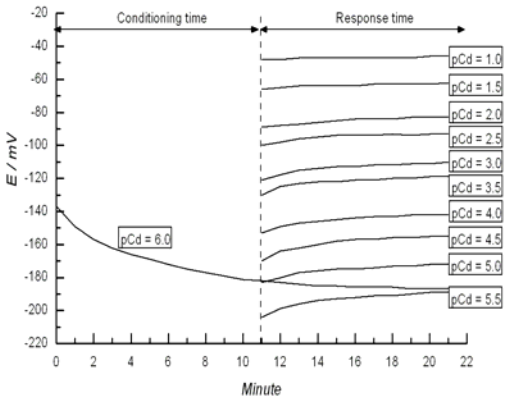

Fig. 6. The variation of the potential of sensor 1 in the 11 solutions of control set.

3.8 Selectivity

In general, for the cation-selective sensors, the K_{MN} constant is given by the relation:

$$E = E^{\circ} + \frac{2{,}303RT}{zF} \lg\left[a_M^{m+} + K_{MN} \cdot \left(a_N^{n+}\right)^{m/n}\right]$$

For values of $K_{MN} < 1$, the sensor favours the primary ion, M^{m+}, over the interfering (secondary) one, N^{n+}, at least as concerns selectivity.

There are various methods for assessing selectivity based on potential measurements in separate solutions and mixed ones, respectively, of the primary and interfering cations. Determination of the cadmium-selectivity constant of the sensor, in the presence of lead, will be graphically exemplified by:

IA. the separate solutions method –
assessment of selectivity's in the values of potentials;
IB. the separate solutions method –
assessment of selectivity's in the values of activities;
IIA. the mixed solutions method –
the activity of the primary cation is varied while the the
activity of the interfering cation is kept constant;
IIB. the mixed solutions method –
the activity of the primary cation is kept constant while
the activity of the interfering cation is varied.

Six standard solutions of Cd^{2+} were used, obtained from $Cd(NO_3)_2$, as well as 6 standard solutions of Pb^{2+} obtained from $Pb(NO_3)_2$, with concentrations within the $1 \cdot 10^{-6}$ - $1 \cdot 10^{-1}$ M Cd^{2+} interval and Pb^{2+}, respectively. Ionic strength, J = 0.32 and pH = 4.7 (in acetic buffer) were kept constant. The calibration curves obtained by passing the Cd-ISME based on CdSe through the 6 standard solutions of Cd^{2+} and Pb^{2+}, respectively, as well as the values of the potentials and of the concentrations on the basis of which the selectivity constant, K_{CdPb}, was determined, by the separate solutions methods I A and I B are shown on the graph in Fig. 7.

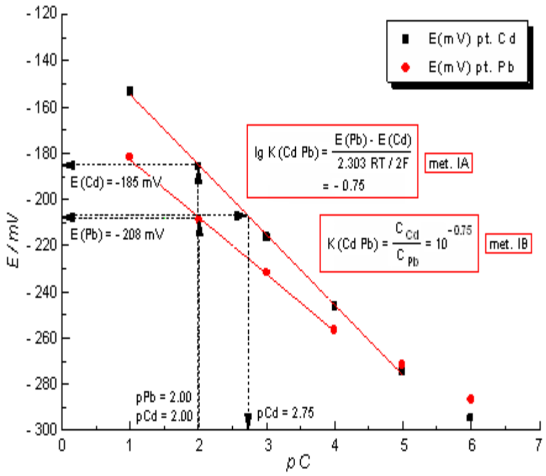

Fig. 7. The determination of the selectivity constant, K_{CdPb} , by the separate solutions method.

Considering that the I B method more correctly expresses the dependence of the selectivity constant on the primary cation concentration, on the one hand, and on the interfering cation concentration, on the other, we propose, in what fallows, an addition to the I B method of selectivity estimation by using separate solutions of the two cations. Thus, by means of some values of the selectivity coefficient exponent, pK_{CdPb} , obtained by the I B method, $pK_{CdPb} = f(pC_{Cd})$ and $pK_{CdPb} = f(pC_{Pb})$, respectively, are graphically represented. Two slops are obtained, as shown in Fig. 8.

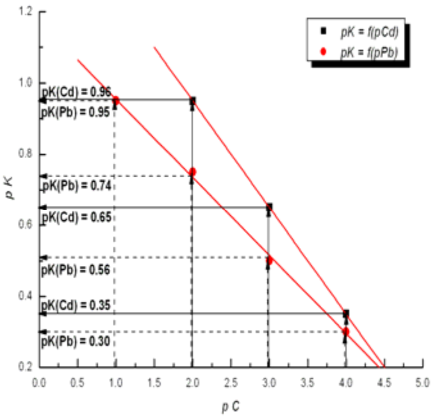

Fig. 8. The selectivity coefficient exponent, $pK_{CdPb} = f(pCd)$ and $pK_{CdPb} = f(pPb)$.

This graphic representation allows the rapid determination of the selectivity constant and, from its expression, of the interfering cation Pb^{2+} concentration at which interference occurs, in a solution of a certain concentration in the primary Cd^{2+} cation and vice versa. We also consider welcome this addition to the I B method of the selectivity constant determination in separate solutions because it very well achieves the link with the mixed solutions method in its II A and II B variants.

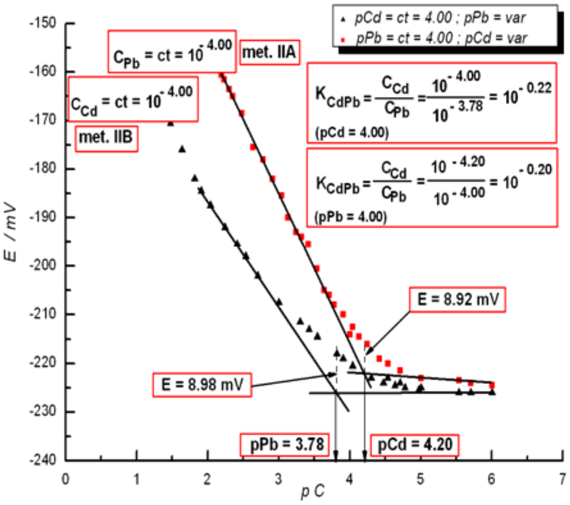

Fig. 9. Determination of the selectivity constant, K_{CdPb}, by the mixed solutions method.

The graphs in the Fig. 9 illustrate the determination of the selectivity constant of a sensor based on CdSe towards Cd^{2+} in the presence of Pb^{2+}, K_{CdPb}, by the II A and II B mixed solutions methods.

The determinations were performed:

1. in a constant and low concentration, $10^{-4,0}$ M Pb^{2+} solution, in interfering cation and a variable one in the primary cation (curve II A);
2. in a constant and low concentration, $10^{-4,0}$ M Cd^{2+} solution, in primary cation and a variable one in the interfering cation (curve II B).

The values of the selectivity coefficients towards the primary cation Cd^{2+}, in the presence of interfering cation Pb^{2+}, of the two sensors, based on selenide and sulphide, respectively, are shown in Table 7.

The table reveals the good correlation between the selectivity coefficients determined for the sensor based on CdSe by both methods, and also the fact that the selectivity constants are subunitary, which means that the sensor shows a good selectivity for the Cd^{2+} cations in the presence of Pb^{2+} cations. Also, the relatively great difference is noticed between the selectivity coefficient determined and those mentioned in literature for the sensor based on CdS and which, actually, differ from one author to another.

Table 7. The selectivity coefficients, pK_{CdPb}, for sensors based on CdSe and CdS, respectively.

pC	pK_{CdPb} for the sensor based on selenide			pK_{CdPb} for the sensor based on sulphide		
	IB*	IIA	IIB	IIB	[16]	[16]
$pC_{Pb} = 4.0$	0.30	0.20	-	-	-	-
$pC_{Cd} = 4.0$	0.35	-	0.22	0.90	0.78	0.30
$pC_{Pb} = 3.0$	0.56	0.80	-	-	-	-
$pC_{Cd} = 3.0$	0.65	-	0.40	-	-	-

In the case of zinc and nickel, proceeding similarly, it is noticed that the values of the potential for the interfering cation, Zn^{2+} and Ni^{2+}, respectively, are outside the range of potentials, which represent the response to Cd^{2+}, being more negative over the entire concentrations interval. It can be stated that the Zn^{2+} and Ni^{2+} ions are practically non-interfering in the case of the utilization of the Cd-selective sensor based on selenide.

Also, unlike in the situation in the case of the Pb^{2+} cation, the experiments carried out have demonstrated that the selectivity of the sensor based on CdSe for the Cd^{2+} ions in the presence of Zn^{2+} and Ni^{2+} ions is much better than that of the sensor based on CdS.

Assessment of the selectivity of the sensor based on selenide toward Cd^{2+} in the presence of interfering Co^{2+} and Cu^{2+} ions led to the results shown in Tables 8 and 9.

Table 8. The selectivity coefficients, pK_{CdCo} , sensors based on CdSe and CdS, respectively.

pC	pK_{CdCo} for the sensor based on selenide			pK_{CdCo} for the sensor based on sulphide		
	IB*	IIA	IIB	IIB	[16]	[16]
pC_{Co} = 5.0	1.10	1.10	-	-	-	-
pC_{Cd} = 5.0	2.75	-	2.85	-	-	-
pC_{Co} = 4.0	1.70	1.80	-	-	-	-
pC_{Cd} = 4.0	4.30	-	3.40	2.95	1.69	4.30

Table 9. The selectivity coefficients, pK_{CdCu} , sensors based on CdSe and CdS, respectively.

pC	pK_{CdCu} for the sensor based on selenide			pK_{CdCu} for the sensor based on sulphide		
	IB*	IIA	IIB	IIB	[16]	[16]
pC_{Cu} = 5.0	-1.50	-1.10	-	-	-	-
pC_{Cd} = 5.0	-0.50	-	-0.90	-	-	-
pC_{Cu} = 4.0	-2.90	-	-	-	-	-
pC_{Cd} = 4.0	-1.10	-	-1.30	-0.10	-	-

The subunitary values obtained by any method for pK_{CdCu} , and the high supraunitary values of K_{CdCu} , respectively, shown that there exists a strong interference of the Cu^{2+} cation and this will always hinder the determination of the Cd^{2+} cation by means of a Cd-selective solid membrane sensor.

3.9 Analytical determination of cadmium from real samples

For the determination of cadmium from real samples, the experiments were carried out by a sensor with the optimum composition of the membranous mixture, 30 % CdSe + 70 % Ag_2S. The potentiometric determination of cadmium in galvanic water was carried out by standard addition potentiometry method with a Cd^{2+} ion-selective sensor. The results were compared with a spectrophotometric method for cadmium determination. The experimental data are showed in table 10.

As it can be seen from table 10 there is a good agreement between the potentiometric and spectrofotometric results showing that the cadmium-selective sensor based on cadmium selenide is analytically useful for the determination of cadmium in galvanic water and other real samples. The recovery tests for samples, by potentiometry with the sensor, are situated in range 97.14 – 101.04.

Table 10. Comparative results of the cadmium from galvanic water determination through potentiometry and spectrofotometry.

Sample	Cadmium determination		
	Potentiometric method	Spectrophotometric method	Recovery (%)
Sample 1*	2.92 ± 0.07	2.89 ± 0.03	101.04
Sample 2**	1.80 ± 0.08	1.79 ± 0.04	100.56
Sample 3***	0.34 ± 0.01	0.35 ± 0.01	97.14

* Sample 1 - wash waters of cadmium covered pieces
** Sample 2 - mixed galvanic waters
*** Sample 3 - treated and sloped waters

4. Conclusions

The studies presented in the present paper have led to the building of a new type of solid, multilayered membranous material based on selenide, used for achieving a Cd-selective sensor. Following the experiments carried out, the conclusion has been reached that the optimum membrane contains 30% CdSe + 70% Ag_2S and does not require thermal processing either before or after tablet formation. Under the optimum working conditions established for the sensors obtained with this membrane (10 minutes conditioning in the most diluted solution of the standardization set), they prove a Nernstian behaviour within the $1\cdot10^{-6}$ - $1\cdot10^{-1}$ M Cd^{2+} concentration range, and a response time of 1-2 minutes, function of the cadmium ion concentration. The periodical conditioning of the membrane surface by wet and abrasive grinding allows these sensors to be used in optimum parameters for a long time. The studies carried out have also demonstrated a good selectivity of the sensor based on selenide toward Cd^{2+} cation in the presence of the Pb^{2+}, Ni^{2+}, Zn^{2+} and Co^{2+} cations. The only iterferent that raises problems, especially at low concentrations of the primary ion, is Cu^{2+}.

By comparison with the “classical” sensor based on sulphide, the sensor based on selenide has proved to be more effective as regards the detection limit, improved by a decade, and as regards the selectivity towards the primary cation in the presence of some interfering cations.

It is very easy to construct, has a higher mechanical resistance and can be easy regenerated.

The electrode, successfully tested for the determination of cadmium in galvanic water, exhibits suitable characteristics for routine analysis of cadmium in real samples.

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