Ion-selective Membrane Electrodes for the Determination of Heavy Metals

Construction characterization and applications

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This paper presents the construction and characterization of some ion-selective membrane electrodes (ISE) for the determination of the following cations Cu^{+2}, Cd^{+2}, Ni^{+2}, Pb^{+2}, and Hg^{+2} in a PVC matrix using as electroactive material acetoacetanilide, dicyclohexan-24-crown-8, dibenzo-18-crown-6, dicyclohexyl-18-crown-6 or poly-(4-vinyl pyridine). For each electrode the following characteristics have been established: linear response range, limit of quantification, response time and selectivity. The electrodes were used for the in vitro potentiometric determination of traces of heavy metals in some aqueous extracts orally administered for therapeutic purposes.

Keywords: ISE, potentiometry, heavy metals.

Heavy metal toxicity is a clinically significant medical condition that improperly treated may result in significant morbidity and mortality. Heavy metals may enter the body orally, through inhalation, or skin absorption. Body part and severity of damage varies with the metal involved, the route it has entered the body, patient age and level of toxicity.

Ion-selective membrane electrodes (ISE) play an important part in chemical analysis due to their simplicity, speed and accuracy when compared to other analytical methods. High selectivity allows their use for the determination of numerous organic and inorganic compounds without prior separation [1-5].

Review of the *literature discloses* the use with good results of membrane ion selective electrodes for the determination of heavy metals from various media [6-10].

In this study ion-selective membrane electrodes with PVC matrix were constructed and characterized for the determination of cations such as Cu^{+2}, Cd^{+2}, Ni^{+2}, Pb^{+2} and Hg^{+2}.

Experimental part

Materials and methods

Potentiometric measurements were carried out using a 301 digital Hanna pH/millivoltmeter. The ion-selective membrane electrode was used as indicator electrode in conjunction with a OP-0830P Radelkis saturated calomel electrode(ESC) as reference electrode.

All reagents used while preparing the membranes were produced by Fluka or Aldrich: polyvinyl chloride (PVC), acetoacetanilide (AAA), dicyclohexane-24-crown-8 (DCH24C8), poly-(4-vinyl pyridine) (P4VP), dibenzo-18-crown-6 (DB18C6), dicyclohexyl-18-crown-6 (DC18C6), o-nitrophenyloctyleter (o-NPOE), di(butyl)butylphosphonate (DBBP), dioctylphthalate (DOP), sodium tetraphenylborate (NaTPB) and tetrahydrofuran (THF).

The construction of the electrodes

Selective membrane was obtained after evaporation of THF out of 2mL solution that had been continuously poured into a thin layer inside a 30mm in diameter glass ring mounted on a glass plate. The solution contained various proportions of electroactive compound, plasticizer, PVC powder and additive. Optimal proportions used to obtain homogeneous, thin, elastic and with good mechanical strength membranes are shown in table 1 [11-14].

Discs of suitable diameter had been cut from the obtained membrane in order to be applied at the end of a PVC tube of 10mm inner diameter using a PVC and THF mixture as a binder and it was allowed to dry for 24 h. The body of the electrode that had the selective membrane attached to, was filled with internal reference solution and then the Ag/AgCl internal reference electrode was immersed. A solution of analyte salt that the electrode was selective to, was used as internal reference solution in a concentration of 10^{-3}mol/L in AgCl saturated solution.

In order to obtain the Ag/AgCl electrode, a 1mm in diameter and 50 mm long silver wire was used after it had previously been cleaned with concentrated HNO_3 and then rinsed with distilled water. The silver wire constituted the anode of an electrolysis cell, while the cathode was a platinum plate. The electrode assembly was placed in a AgCl saturated solution and then it was connected to a 9V battery with a 1Mohm resistance to give a 10μA current. Thus a compact and uniform layer of AgCl was deposited on the surface of the silver wire.

Electrode	Electroactive compound	Plasticizer	Additive	Matrix
Cu^{+2} ISE	AAA (1)	*o*-NPOE (67)	NaTPB (1)	PVC (31)
Cd^{+2} ISE	DCH24C8 (1)	DBBP (67)	NaTPB (1)	PVC (31)
Ni^{+2} ISE	DB18C6 (1)	DOP (67)	NaTPB (1)	PVC (31)
Pb^{+2} ISE	DC18C6 (1)	*o*-NPOE (67)	NaTPB (1)	PVC (31)
Hg^{+2} ISE	P4VP (1)	DOP (67)	NaTPB (1)	PVC (31)

Table 1
MASS PERCENTAGE COMPOSITION OF PVC MATRIX ION-SELECTIVE MEMBRANES

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Before the measurements, the selective electrode membrane had been conditioned by immersion in a 10^{-5}mol/L analyte salt solution for 120 minutes, after which it was rinsed thoroughly with distilled water. When not in use the electrode was stored dry.

The electrochemical cell included as external reference electrode a saturated calomel electrode (SCE).

Results and discussions

pH effect

The effect of *p*H on electrode response was examined by measuring the potential variation of the electrochemical cell with three solutions of various concentrations (10^{-4}, 10^{-3} and 10^{-2}mol/L). The response of the electrodes to 10^{-3}mol/L solution in the 1.0-9.0 *p*H range is shown in figure 1.

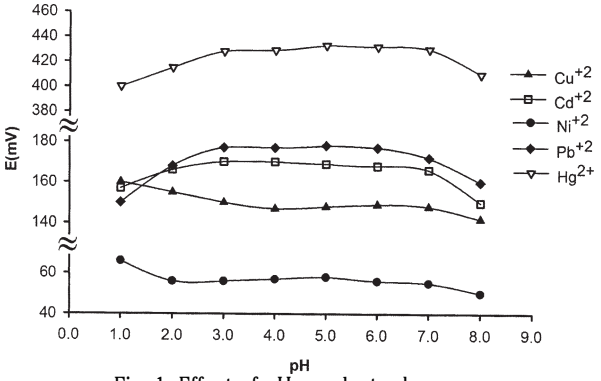

Fig. 1. Effect of pH on electrode response

The working technique for the *in vitro* determination of trace heavy metals in aqueous extracts orally administered for therapeutic purposes has imposed the need to do all determinations at *p*H 7.0.

Total ionic strength

A 0.1 value for the ionic strength was found to be optimum for samples with concentrations below 10^{-1} mol/L and it was obtained by dilution using 1mol/L KNO_3. The measured potential was not influenced by ionic strength for 10^{-2} and 10^{-1}mol/L solutions.

Response time

The response time varied depending on the analyte concentration and it did not depend on whether the potentials were recorded from low to high concentrations or vice versa. For low concentrations the response time was within 45 s while the electrodes response to high concentrations was virtually instantaneous in all cases.

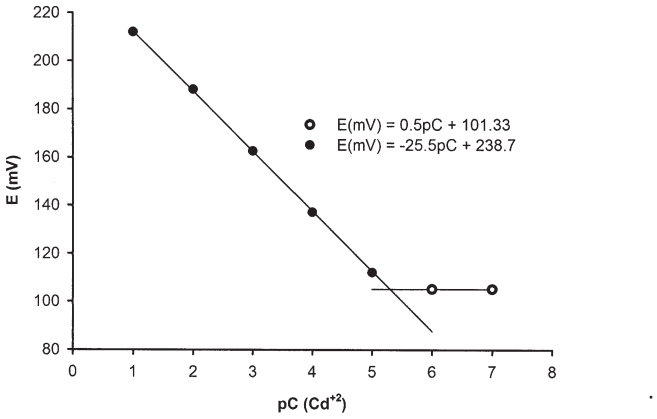

Fig. 2. LOQ and calibration curves for Cd^{+2} ISE

Experimental data obtained were subject to statistical processing, establishing for each constructed electrode its linear response range, limit of quantification, precision, accuracy, selectivity and robustness of the method [15, 16].

Linearity

The electrodes response was studied in the concentration range between 10^{-7}-10^{-1}mol/L at *p*H 7.0 and 0.1 ionic strength (E = mV, C = mol/L, pC = - log C). For each electrode the concentration range of linear relationship between the measured potential and the concentration of the analyzed ion was determined (table 2).

A graphical method was applied to calculate the limit of quantification (LOQ) defined as the intersection of the regression line for the linear domain with the range when the electrode response was relatively constant [17]. An example is shown in figure 2 for Cd^{+2} ISE.

Precision

The precision of the method was studied in terms of repeatability and reproducibility. There have been two series of measurements in various days for three different concentrations of analyte 10^{-4}, 10^{-3} and 10^{-2}mol/L. For each concentration level three determinations series were carried out (table 2).

Accuracy

The accuracy of the electrodes was assessed by analyzing three standard solutions of 10^{-4}, 10^{-3} and 10^{-2}mol/L respectively, following the correspondence between the real and the analytical result obtained from measurements by calculating the relative error, Xd (%), using the equation:

Electrode		Cu^{+2} ISE	Cd^{+2} ISE	Ni^{+2} ISE	Pb^{+2} ISE	Hg^{+2} ISE
Linearity range		10^{-2}-10^{-6}mol/L	10^{-1}-10^{-5}mol/L	10^{-1}-10^{-5}mol/L	10^{-2}-10^{-6}mol/L	10^{-2}-10^{-6}mol/L
Regression		E = 20.3·pC+ 208.4	E = -25.5·pC+ 238.7	E = 23.8·pC+ 13.6	E = -19.1·pC+ 233.6	E = 32.6·pC+ 328.8
Correlation coefficient (r^2)		0.9986	0.9948	0.9982	0.9982	0.9939
Slope		20.3mV/decade	25.5mV/decade	23.8mV/decade	19.1mV/decade	32.6mV/decade
Standard deviation (σ)		0.4676	0.9295	0.4393	0.1516	0.3386
LOQ		$3.63\cdot10^{-7}$mol/L	$5.62\cdot10^{-6}$mol/L	$4.57\cdot10^{-6}$mol/L	$3.16\cdot10^{-7}$mol/L	$7.08\cdot10^{-7}$mol/L
Repeatability I st Series	SD	3.11	3.89	2.04	2.51	2.07
	RSD	3.17%	3.90%	2.05%	2.48%	2.08%
Repeatability II nd Series	SD	3.31	3.62	2.07	1.58	2.23
	RSD	3.36%	3.63%	2.08%	1.57%	2.24%
Reproducibility	SD	3.20	3.65	2.00	2.06	2.09
	RSD	3.25%	3.64%	2.01%	2.04%	2.10%
Accuracy	$\overline{Xd}$	3.26%	3.18%	1.91%	1.69%	2.06%

Table 2
VALIDATION PARAMETERS OF POTENTIOMETRIC DETERMINATION METHODS FOR Cu^{+2}, Cd^{+2}, Ni^{+2}, Pb^{+2} AND Hg^{+2} USING ISE

Interferer	Cu^{+2} ISE	Cd^{+2} ISE	Ni^{+2} ISE	Pb^{+2} ISE	Hg^{+2} ISE
Cu^{+2}	-	$2.2 \cdot 10^{-2}$	$2.1 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	$4.5 \cdot 10^{-3}$
Cd^{+2}	$1.4 \cdot 10^{-2}$	-	$3.2 \cdot 10^{-2}$	$1.0 \cdot 10^{-3}$	$4.4 \cdot 10^{-3}$
Ni^{+2}	$3.0 \cdot 10^{-2}$	$2.0 \cdot 10^{-2}$	-	$4.8 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$
Pb^{+2}	$3.6 \cdot 10^{-2}$	$3.1 \cdot 10^{-2}$	$2.6 \cdot 10^{-3}$	-	$5.7 \cdot 10^{-3}$
Hg^{+2}	$3.1 \cdot 10^{-2}$	$3.5 \cdot 10^{-2}$	$3.1 \cdot 10^{-3}$	$7.8 \cdot 10^{-3}$	-
Zn^{+2}	$7.8 \cdot 10^{-3}$	$2.7 \cdot 10^{-2}$	$7.1 \cdot 10^{-3}$	$3.9 \cdot 10^{-4}$	$3.5 \cdot 10^{-3}$
Al^{+3}	$3.9 \cdot 10^{-3}$	$3.9 \cdot 10^{-2}$	$2.1 \cdot 10^{-3}$	$3.1 \cdot 10^{-3}$	$7.1 \cdot 10^{-3}$
Co^{+2}	$2.1 \cdot 10^{-2}$	$2.1 \cdot 10^{-2}$	$9.1 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$	$4.5 \cdot 10^{-4}$
Cr^{+3}	$4.2 \cdot 10^{-3}$	$3.5 \cdot 10^{-2}$	$1.8 \cdot 10^{-3}$	$5.1 \cdot 10^{-3}$	$1.2 \cdot 10^{-4}$
Fe^{+3}	$1.1 \cdot 10^{-3}$	$5.7 \cdot 10^{-2}$	$1.1 \cdot 10^{-3}$	$6.2 \cdot 10^{-3}$	$4.5 \cdot 10^{-4}$
Mn^{+2}	$2.2 \cdot 10^{-3}$	$3.9 \cdot 10^{-2}$	$3.6 \cdot 10^{-3}$	$3.3 \cdot 10^{-4}$	$6.5 \cdot 10^{-4}$
Ca^{+2}	$2.3 \cdot 10^{-3}$	$6.1 \cdot 10^{-2}$	$1.0 \cdot 10^{-2}$	$5.2 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$
Mg^{+2}	$2.2 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$	$9.0 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	$5.3 \cdot 10^{-4}$
Na^{+}	$4.4 \cdot 10^{-2}$	$2.2 \cdot 10^{-1}$	$6.0 \cdot 10^{-3}$	$4.0 \cdot 10^{-3}$	$3.5 \cdot 10^{-3}$
K^{+}	$3.3 \cdot 10^{-2}$	$2.4 \cdot 10^{-1}$	$4.4 \cdot 10^{-3}$	$3.1 \cdot 10^{-2}$	$4.5 \cdot 10^{-3}$

Table 3
SELECTIVITY COEFFICIENT (K)

$$Xd(\%) = \frac{|Xr - Xa|}{Xa} \cdot 100 \quad (1)$$

where Xr was the value calculated from the calibration curve for the theoretical value Xa (table 2).

Robustness

The robustness of the methods was assessed by comparison of the intra and inter-day assay results measured by two analysts under a variety of conditions such as small changes of laboratory temperature and provenience of chemicals. The percent recoveries were good.

Electrode selectivity

The selectivity of electrodes was investigated by the separate solution method and the potentiometric selective coefficients (K), were calculated by equations (2) and (3) [18]:

$$\log K = \frac{E_{(II)} - E_{(I)}}{P} + \log[A^{y+}] - \log[I^{z+}] \quad (2)$$

$$K = 10^{\frac{\Delta E}{P}} \cdot \frac{[A^{y+}]}{[I^{z+}]} \quad (3)$$

Two 10^{-3}mol/L separate solutions were prepared for the primary ion (A^{y+}) and the interfering secondary ion (I^{z+}). Their potentials E_I (for A^{y+}) and E_{II} (for I^{z+}) were measured (P - slope of the calibration curve).

Life span of the electrodes

The electrodes used constantly during the experiment had an average duration of use of approximately 5-6 weeks.

Analytical applications

The constructed electrodes were used to quantifying the bioavailability of heavy metals in some aqueous extracts in a simulated digestive system [19]. To that end the plant extract was adjusted to *p*H 2.0 with HCl, swine pepsin was added and incubated for 1 h at 37°C. It was then brought to *p*H 5.6 with $NaHCO_3$ a mixture of pancreatin, porcine bile extract and lipase was added, the *p*H was adjusted to 7.0 using NaOH and the mixture was incubated for 2 h at 37°C. The amount of free metal was determined using the standard addition method. The results will be the subject of a future scientific report.

Conclusions

A series of ion-selective PVC matrix membrane electrodes for the determination of Cu^{+2}, Cd^{+2}, Ni^{+2}, Pb^{+2} and Hg^{+2} was built. The electrodes were studied from the point of view of main functional characteristics and they were used for the determination of trace of heavy metals from aqueous extracts. The proposed methods were simple fast and accurate.

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