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Thiocyanate and fluoride electrochemical sensors based on nanostructurated metalloporphyrin systems

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Metalloporphyrins such as Rh(III)TPPCl and Zr(IV)TPPCl$_2$ [1] were used as ionophores to prepare nanostructurated polymeric membrane sensors for thiocyanate and fluoride. Results from potentiometric experiments suggest the optimal membrane composition with these molecular systems [2] which is essential to improve the selectivity and the stability of the potentiometric response of the sensors. Sensors prepared exhibit rapid, fully reversible and Nernstian response towards thiocyanate and fluoride, in the large concentration range Two functional model of the sensors with internal solid contact and internal liquid (filling solution) contact were elaborated and tested. Their optimal construction is simple and robust enough. The sensors were successfully tested for monitoring thiocyanate and fluoride.

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1. Introduction

A large number of ion selective solvent polymeric or liquid membrane sensors have been developed during the last time. A comprehensive list of such sensors up to 1990 can be found in Umezawa handbook [3] The membranes of the sensors are typically based on a polymer such as polyvinyl chloride (PVC) or polyurethane and usually also contain a water immiscible organic liquid which has plasticizer properties. In order to measure the potential, the membrane must be assembled into an electric circuit. One surface of the membrane contacts the sample solution, while the other surface is electrically connected, via internal reference, to the potentiometric measurement equipment, which is further connected through a reference electrode to the sample solution. The internal reference may be a solid (platinum, copper wire and silver wire, graphite), which directly contacts the ion selective membrane (the membrane can by directly deposited on a conductive support). So far, most commonly an electrolyte is applied at the inner membrane side, which is contacted to a reference electrode.

Over the past 15 years, considerable effort has been placed on the development of new solvent/polymeric membrane sensors suitable for the potentiometric determination of anionic species [4]

The solvent polymeric membrane sensor for determination of different analytes has been described so far [5] and these types of chemical sensors is the widest known. Due to their ability, metallophthalocyanines[6], and metalloporphyrins [7-11] appear as one of the most classes of compounds to be used as the anion-selective materials. Solvent polymeric membrane sensors based on metalloporphyrins are widely used for potentiometric analysis of different anions [12] and tends to become a promising and robust instrument for complex analysis.

The construction of the sensors is a very interesting development in the field of ion-selective sensors. Coated type ion-selective sensors [13] have opened a new route toward all solid state carrier-based ion-selective electrodes. These sensors can be applied in flowing streams and as micro sensors. They are very easy to construct, have a higher mechanical resistance and can be easy regenerated. The solid electrical contact sensors have been used in flow injection analysis and direct or indirect determination of many ion species.

The purpose of the present work was to investigate the effect of construction of the sensors for thiocyanate and fluoride, based on the metalloporphyrins such as Rh (III) TPPCl and Zr(IV)TPPCl, on the response characteristics and their analytical applications.

Membrane sensors formulation and its optimization have been recently reported [14, 15].

Thiocyanate is major toxic metabolite of hydrogen cyanide, as a result of cigarette smoking or industrial pollution. Thiocyanate represents a product of tobacco that accumulates in blood and tissues of smokers. The toxicity of thiocyanate is significantly less than that of cyanide, but chronically elevated levels of blood thiocyanate can inhibit the uptake of iodine by the thyroid gland.

Fluoride is an important anion, present in various environmental, clinical and food samples Small amounts of fluoride are vital for organism, but it is toxic in larger amounts. The lethal dose is 0,20-0,35g per kg body weight. Excessive amounts of fluoride in the form of different compounds can enter in the human body by means of polluted air, water and food chain.

Electroanalytical methods based on potentiometry with ion selective sensors, seem to be the most convenient methods of fluoride and thiocyanate determination [16].

2. Experimental

Reagents:

5,10,15,20-tetraphenylporphyrin-rhodium III)chloride(Rh(III)TPPCl) and 5,10,15,20-tetraphenylporphyrin-zirconium(IV)(Zr(IV)TPPCl$_2$) was synthesized, purified and characterized [1]; PVC of high molecular weight; dioctylphtalate(DOP),o-nitrophenyloctyleter (o-NPOE)from Merck; trioctylmethylammonium chloride(TOMACl), sodiumtetraphenylborate (NaTPB) and tetrahydrofuran (THF) from Fluka; PVC - bar for sensors construction and copper rods as conductive support.

All solutions were prepared from potassium and sodium salts of the given anions in 0,05M 4-morpholinoethanesulfonic acid (MES) at pH 5,5 adjusted with NaOH.

Ion-selective sensor formulation:

Sensors were elaborated in the two functional model with internal solid contact (I) (figure 1 a) and with liquid internal contact (II) (figure 1 b) respectively. The sensor (I) were prepared from copper rods (6 mm diameter and 6mm long) The copper rod was sealed into the end of a PVC tube of about the same diameter by epoxy resin and attached via silver epoxy cement to central wire of the coaxial cable. The working surface (copper rod) of the sensor was polished with fine alumina slurries on a polishing cloth, washed and allowed to dry. The copper rod of the sensor was dipped into the optimal membrane solution (which were prepared by dissolving of all components and thorough mixing), for a several times and the solvent was slowly evaporated overnight (48 hours). The sensitive membrane was formed on the copper rod surface.

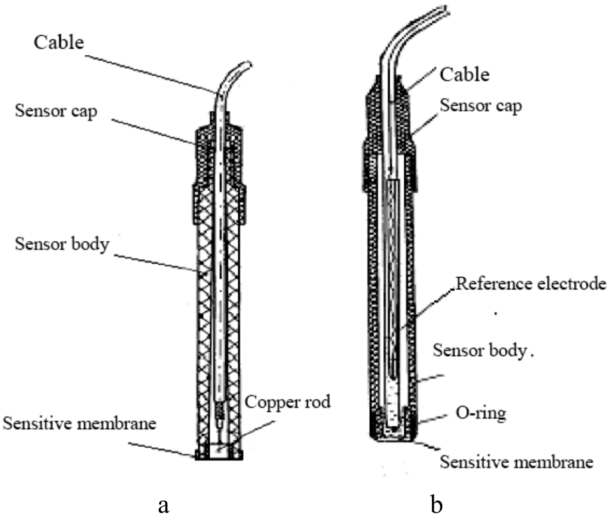


Fig. 1 .Scheme of the sensor: a- sensor (I) b- sensor (II).

Membranes employed to construct the sensor (II) consisted of the optimal membrane composition for each anions. The resulting mixture was poured into rings placed on a smooth glass plate.for 48 hours and THF was allowed to evaporate to overnight, leaving an approximately 0,15 mm – thich of the membrane. Six mm diameter discs were cut out from this membrane and mounted in a PVC sensor bodies by a special O-rings. Sodium thiocyanate 0,01 mM, sodium chloride 10mM and sodium fluoride 0,01M in MES pH = 5,5, inner solution were used. The thiocyanate sensor(I) and (II) were equilibrated for 24 h in 0,01 mM sodium thiocyanate and 10mM sodium chloride solution. And the fluoride sensor(I) and (II) in a 0,01 M sodium fluoride respectively. All measurements were performed at 22±2 oC. Potentials were measured using a Hanna Instruments HI8817 pH/mV-meter. The following cell assembly:

Hg,Hg$_2$Cl$_2$,KCl(saturated)//sample solution/ membrane/copper rod surface, for sensor (I) and Hg,Hg$_2$Cl$_2$,KCl(saturated)//samplesolution/ membrane/inner filing solution/AgCl/Ag
for sensor (II).

3. Results and discussion

In order to investigate the effect of the sensor type (construction) on the potentiometric response characteristics three sensors of (I) and (II) type, for thiocyanate and fluoride were prepared, with the optimal composition membranes.

The optimal composition membranes: Rh(III)TPPCl 1wt% : DOP 66 wt % : PVC 33wt% and TOMACl 20 mol%(relative to Rh(III)TPPCl) for thiocyanate sensor and Zr(IV)TPPCl 1wt%: o-NPOE 66wt%:PVC 33wt%: NaTPB 20 mol%(relative to Zr(IV)TPPCl) for fluoride sensor were used.

The response parameters of the sensors such as: working range, slope, and the selectivity were followed.

The reproducibility of the response characteristics of the sensor type (I) are shown in figure 2 and the evolution of the response characteristics in time of the sensor type (II) are presented in figure 3a, b.

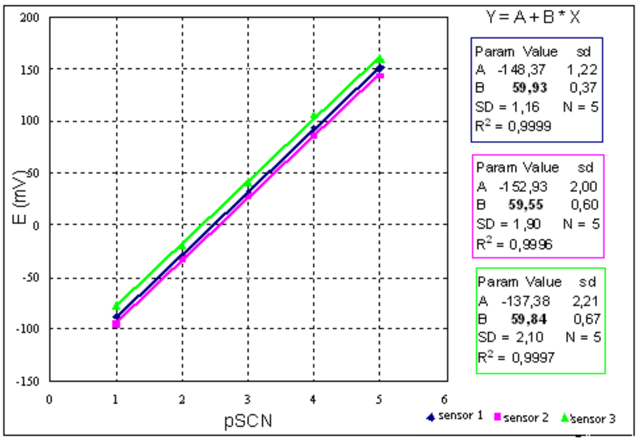
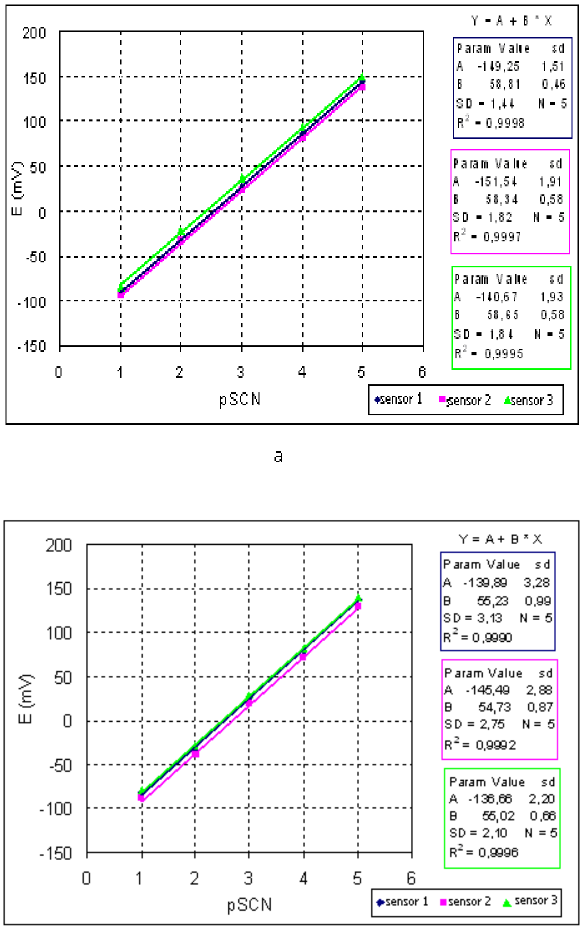


Fig. 2. Response characteristics of the sensor (I).



a

b

Fig. 3 Response characteristics of the sensor (II) in time
a) after two weeks b) after a month.

As it can be seen from figures 2 the reproducibility of the functional parameters of the sensors are good. A little decrease of the slope sensor(II) (figure 3) in time was showed, but remains after a month of intensive use in the analytical useful range.

Comparative values of the selectivity coefficients (investigated by SSM) for both types of sensors are shown in table 1.

Table 1 Comparative value of the selectivity coefficients.

Interfering anion, X^-	Selectivity coefficients,$\log K_{A^-,X^-}$			
	Sensor (I)		Sensor (II)	
	SCN-ISE	F-ISE	SCN- ISE	F-ISE
SCN^-	0.00	-1.19	0.00	-1.15
ClO_4^-	-0.71	-0.66	-0.80	-0.70
Sal^-	-1.96	+2.46	-1.88	+2.41
I^-	-1.39	-1.38	-1.29	-1.24
NO_3^-	-2.87	-2.31	-2.94	-2.37
NO_2^-	-1.71	-1.47	-1.65	-1.37
Br^-	-3.51	-2.40	-3.58	-2.35
Cl^-	-3.71	-2.92	-3.65	-2,65
F^-	-3.80	0.00	-3.84	0.00

As it can be seen from table 2, the values of the selectivity coefficients for both types of the sensors are comparable.

The evolution of sensor (I) in time is presented in Table 2.

Table2 The slope of the sensor (I) in time

Time of use	*The slope, mV/pC	
	SCN^- - ISE	F^- - ISE
Two weeks	59.5	90.6
A month	58.5	89.5

*average of three experiments

The results from table 2 confirmed a small decreased of the slope in time of use the sensor (I) in the same condition of measurements.

The main functional parameters (the working range, slope and limit of detection) of the electrodic function for sensor (I) and sensor (II) for the thiocyanate anion are shown in table 3.

Table 3. Comparative response characteristics of the sensor (I) and (II)

Sensor type	SCN- ISE		
	Working range M	Slope, mV/decade	Limit of detection M
Sensor **(I)**	10^{-1}-10^{-5}	59.8	7.10^{-6}
Sensor **(II)**	10^{-1}-10^{-5}	58.5	5.10^{-6}

*average of three determination with each type of sensor

From table 3 it can be seen that: the working range, slope and the limit of detection are comparable values, for the both type of the sensor.

Analytical determination of thiocyanate and fluoride:

For determination of thiocyanate and fluoride in urine samples from smoker and non-smoker patiens, the experiments were carried out by sensor (I) and (II) type. The potentiometric determination of thiocyanate and fluoride in urine were carried out by standard addition potentiometry method with SCN^- and F^- ion-selective sensor. The results were compared with a spectrophotometry method for thiocyanate and a gas cromathography method for fluoride. The experimental data are showed in table 4

Table 4. Results of thiocyanate and fluoride determination in urine.

Urine sample/ sensor type	Smoker*		Non-smoker*	
	SCN^- mg/l	F^- mg/l	SCN^- mg/l	F^- mg/l
Sensor (I)	52.263^a (2.2%)	1.821^a (3.5)	18.001^a (6.1%)	0.845^a (5.0%)
Sensor (II)	51.682^a (3.2%)	1.857^a (5.5%)	17.821^a (6.9%)	0.922^a (3.6%)
	53.424^b		19.163^b	
		1.760^c		0.890^c

*average of three samples
a- Standard addition potentiometry
b- spectrophotometry
c- Gas cromatography
(RSD%)

As it can be seen from table 4 there is a good agreement between the potentiometric results and the reference methods for sensor (I) and (II) types and for both anions.

4. Conclusions

The construction of the sensor (internal solid contact and internal liquid contact) are not influenced significantly their potentiometric response features.

The potentiometric response features of the sensors not depend by their electrical internal contact. But, the elimination of the inner solution favored and easy increased lifetime and reproducibility of the sensors.

The much simple design of the sensor I are additional desirable feature that have led to their more general use.

The sensor I can be designated for dealing with various measuring situation, such as small sample sizes (micro sensors), flowing samples and muscle fluids.

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

The both types of sensor exhibit suitable characteristics for routine analysis of thiocyanate and fluoride.

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