

## PREPARATION AND PROPERTIES OF THIOCYANATE SOLID-STATE HOMOGENEOUS MEMBRANE ELECTRODES

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*A simple procedure for the preparation of thiocyanate selective membrane electrodes with internal liquid contact is described.*

*The electrodes consist of pellets made from the AgSCN or the mixture of AgSCN and Ag<sub>2</sub>S by using pressure at room temperature.*

*The analytical behaviour of these electrodes is described in terms of potential-concentration curves, selectivity ratios, effect of pH, response time and potentiometric titrations.*

**Key words:** homogeneous thiocyanate-selective electrode

### INTRODUCTION

Ion-selective electrodes have undergone a remarkable development in the last 20 years [1, 2]. These electrochemical sensors have hitherto found numerous applications in direct potentiometry, potentiometric titrations, kinetics studies, biochemistry and biomedical research, industrial analytical control, etc. [1, 3-5].

Various types of ion-selective electrodes are now prepared in many laboratories and produced by some companies.

Ion-selective solid-state electrodes can be manufactured with homogeneous or heterogeneous membrane.

There are data about thiocyanate homogeneous membrane electrodes made with crystalline material by using pressure at an elevated temperature [6, 7], and about thiocyanate heterogeneous membrane electrodes made with crystalline material dispersed in a thermoplastic polymer such as polythene or metacrylic esters [8].

This paper describes the preparation and properties of thiocyanate solid-state homogeneous membrane electrodes based on AgSCN or AgSCN/Ag<sub>2</sub>S.

### EXPERIMENTAL PROCEDURE

#### Chemicals and solutions

All chemicals used were of analytical-reagent grade, produced by Merck or Alkaloid-Skopje.

Solutions of known concentration (0.1 mol · dm<sup>-3</sup> AgNO<sub>3</sub>, 0.1 mol · dm<sup>-3</sup> KSCN) were prepared by standard procedures [9, 10].

The ionic strength of the solution (I = 0.1 mol · dm<sup>-3</sup>) during the recording of calibration curves of the electrodes and in direct potentiometric determinations was kept constant by the addition of potassium nitrate.

#### Apparatus

Measurements were performed by the use of the Orion Research digital analyzer model 801A and

Radiometer saturated calomel electrode model K401 with a potassium nitrate salt bridge. The temperature of the solution was kept constant with a MLW Ultra-termostate model U-15-C. The solution was stirred magnetically.

#### Preparation of membrane electrodes

The silver salts used in the preparation of membrane electrodes were prepared in our laboratory.

Silver thiocyanate was prepared as follows:

A solution of silver nitrate (2.0 g) in double-distilled water (40 cm<sup>3</sup>) was added dropwise with constant stirring to a solution of potassium thiocyanate (1.0 g) in double-distilled water (400 cm<sup>3</sup>). The precipitated silver thiocyanate was left to digest for 24 hours, after

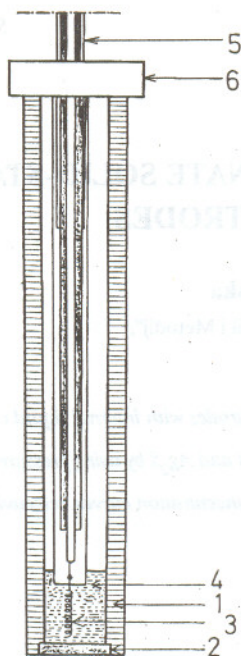


Fig. 1 – Schematic of a thiocyanate-selective electrode with a liquid internal contact: 1 – Electrode body; 2 – Membrane; 3 – Silver wire; 4 – Internal solution; 5 – Connecting wire; 6 – Electrode cap

which it was filtered off, washed with double-distilled water until the filtrate gave no positive reaction for

silver ions, dried at 105°C, ground in an agate mortar and passed through a JEL, DIN N<sup>o</sup> 140E sieve.

Silver sulfide was prepared according to the procedure given by Camman and Rechnitz [11]. After drying at 110°C the precipitated silver sulfide was treated in the same manner as described for silver thiocyanate.

The membranes of electrodes were prepared in the following way:

I) from the silver thiocyanate

II) from the mixture of silver thiocyanate and silver sulfide (in ratios from 30% : 70% to 70% : 30%).

All pellets were formed at 19 MPa pressure at room temperature over a period of 20 hours.

After that the membranes obtained were polished with alumina powder and then with Orion polishing strips. The prepared membranes were set into the respective bearing at the end of a polyvinyl chloride tubing of 15 cm length whose inner and outer diameters were 10.0 and 15.0 mm respectively (Fig. 1).

The internal liquid contact was made by silver wire in a solution of silver nitrate ( $10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ ). The electrodes were stored in a  $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$  thiocyanate solution, which was replaced with a freshly prepared solution every 10–15 days.

## RESULTS AND DISCUSSION

In the course of these investigations eleven electrodes were prepared and evaluated: five electrodes in whose membranes only silver thiocyanate was incorporated (group I electrodes) and six electrodes in whose membranes a mixture of silver thiocyanate and silver sulfide was incorporated (group II electrodes).

The analytical behaviour of these electrodes is described in terms of potential-concentration curves, selectivity ratios, effect of pH, response time and potentiometric titrations.

The calibration curves in standard solutions of  $\text{SCN}^-$  and  $\text{Ag}^+$  ions respectively, with ionic strength  $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ KNO}_3$ , were recorded and the Nernstian limit, detection limit, standard potential and the slope of calibration curves were determined. The form of calibration curves for two electrodes respectively is given in the Fig. 2.

The standard potential of the electrodes prepared was positive: the standard potential of the group I electrodes was 160–190 mV and that of the group II electrodes was 190–208 mV.

The lower limit of their Nernstian response (Nernstian limit) was from  $5.0 \cdot 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$  to  $2.0 \cdot 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$  of the group I electrodes and from

$6.0 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$  to  $3.0 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$  of the group II electrodes. Their detection limit [3] was from  $6.0 \cdot 10^{-7} \text{ mol} \cdot \text{dm}^{-3}$  to  $4.0 \cdot 10^{-7} \text{ mol} \cdot \text{dm}^{-3}$  and from  $7.0 \cdot 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$  to  $3.0 \cdot 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$  in both electrode groups respectively.

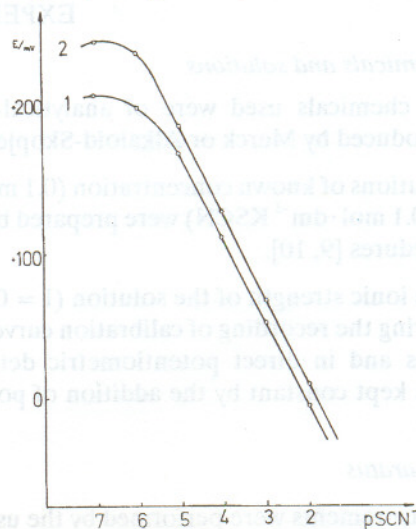


Fig. 2 – Calibration curve of thiocyanate-selective electrode. Electrode membrane contains: 1) 100%  $\text{AgSCN}$ ; 2) 30%  $\text{AgSCN}$  + 70%  $\text{Ag}_2\text{S}$

The slope of calibration curves was 58.0–59.0 mV and 54.0–61.0 mV of the group I and II electrodes respectively.

It can be concluded from these results, that the sensitivity and other electrode functions of both electrode groups are similar, but the group I electrodes displayed some better properties.

Therefore, further investigations have been performed with group I electrodes.

The response time of the electrodes was better than 45 seconds in  $1.0 \cdot 10^{-3}$  mol·dm<sup>-3</sup> thiocyanate solutions as well as in solutions with higher thiocyanate concentrations. In solutions with lower thiocyanate concentrations, however, the response time was not as rapid, but it did not exceed two minutes.

The calibration curves of the prepared electrodes show that they can be successfully applied to the determination of thiocyanate in solutions with concentrations up to  $1.0 \cdot 10^{-5}$  mol·dm<sup>-3</sup> using the direct potentiometric method.

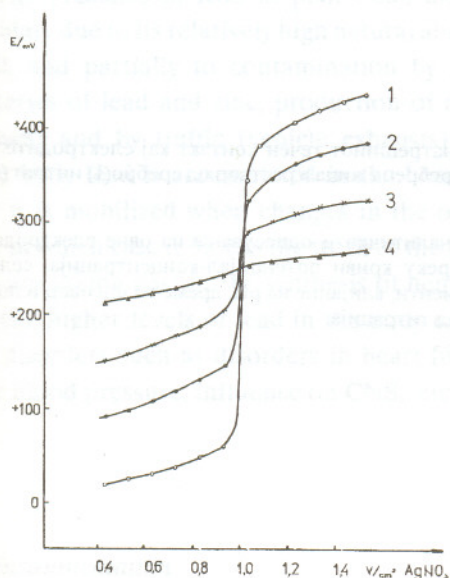


Fig. 3. – Potentiometric titration curves for thiocyanate with silver nitrate solutions:

- 1)  $1.0 \cdot 10^{-2}$  mol·dm<sup>-3</sup> KSCN with  $1.0 \cdot 10^{-1}$  mol·dm<sup>-3</sup> AgNO<sub>3</sub>
- 2)  $1.0 \cdot 10^{-3}$  mol·dm<sup>-3</sup> KSCN with  $1.0 \cdot 10^{-2}$  mol·dm<sup>-3</sup> AgNO<sub>3</sub>
- 3)  $1.0 \cdot 10^{-4}$  mol·dm<sup>-3</sup> KSCN with  $1.0 \cdot 10^{-3}$  mol·dm<sup>-3</sup> AgNO<sub>3</sub>
- 4)  $1.0 \cdot 10^{-5}$  mol·dm<sup>-3</sup> KSCN with  $1.0 \cdot 10^{-4}$  mol·dm<sup>-3</sup> AgNO<sub>3</sub>

The electrodes also displayed a pronounced potential jump at the end point in potentiometric titrations of thiocyanate solutions with silver nitrate (Fig. 3).

These titrations are possible only in solutions with thiocyanate concentrations down to  $1.0 \cdot 10^{-4}$  mol·dm<sup>-3</sup>.

The effect of the pH on the electrode potential was investigated by following changes in the electrode potential with variations in the pH of tested solutions caused by the addition of nitric acid or of sodium

hydroxide solution (Fig.4). The results obtained revealed that pH variations do not affect the potential between pH 5 and 7, so that the electrodes can be safely used in this pH range for thiocyanate determination. But, for concentrations down to  $10^{-4}$  mol·dm<sup>-3</sup> SCN<sup>-</sup>, the pH interval where pH variations do not affect the potential is large (from 3 to 7).

The selectivity coefficients of the electrodes were determined by direct and indirect potentiometric methods [4] in the presence of chlorides, chromates, carbonates, bromides, iodides, arsenates, phosphates and hexacyanoferrate (II), respectively. The values obtained are given in Table I and they are within the expected limits.

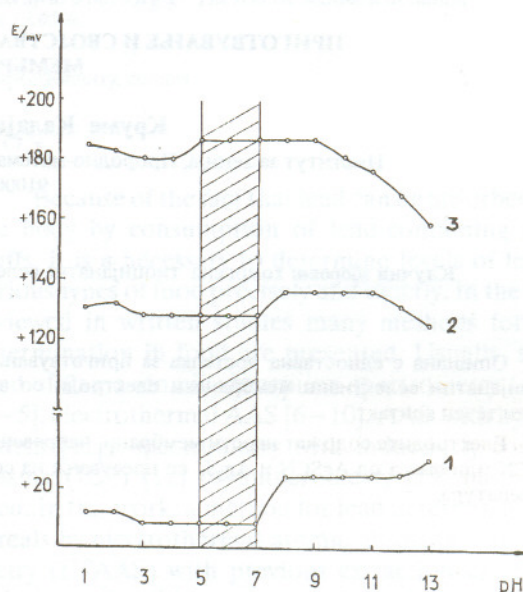


Fig. 4. The effect of the pH on the electrode potential :

- 1.)  $1.0 \cdot 10^{-2}$  mol·dm<sup>-3</sup> KSCN
- 2.)  $1.0 \cdot 10^{-4}$  mol·dm<sup>-3</sup> KSCN
- 3.)  $1.0 \cdot 10^{-5}$  mol·dm<sup>-3</sup> KSCN

Table I

Selectivity coefficients of thiocyanate selective electrode

Interfering ions	$K_{ij}^a$	$K_{ij}^b$
Cl <sup>-</sup>	$3.0 \cdot 10^{-3}$	$8.9 \cdot 10^{-3}$
Br <sup>-</sup>	$5.0 \cdot 10^{-3}$	–
I <sup>-</sup>	3.0	–
CO <sub>3</sub> <sup>2-</sup>	–	$5.4 \cdot 10^{-8}$
CrO <sub>4</sub> <sup>2-</sup>	–	$1.9 \cdot 10^{-7}$
PO <sub>4</sub> <sup>3-</sup>	–	$3.9 \cdot 10^{-7}$
AsO <sub>4</sub> <sup>3-</sup>	–	$4.9 \cdot 10^{-7}$
[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	$3.7 \cdot 10^{-3}$	–

$K_{ij}^a$  – values measured by direct method

$K_{ij}^b$  – values measured by indirect method

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## Резиме

### ПРИГОТВУВАЊЕ И СВОЈСТВА НА ТИОЦИЈАНАТНИ ЦВРСТИ ХОМОГЕНИ МЕМБРАНСКИ ЕЛЕКТРОДИ

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**Клучни зборови:** хомогена тиоцијанатна селективна електрода

Опишана е едноставна постапка за приготвување на тиоцијанатни селективни мембрански електрооди со внатрешен течен контакт.

Електродите содржат цврсти мембрани, направени од AgSCN или смеса од AgSCN и Ag<sub>2</sub>S, со пресување на собна температура.

Внатрешниот течен контакт кај електродите е остварен со сребрена жица и раствор од сребро(I) нитрат ( $10^{-2}$  mol · dm<sup>-3</sup>).

Аналитичкото однесување на овие електрооди е опишано преку криви потенцијал-концентрација, селективни коефициенти, влијание на рН, време на одговор и потенциометриска титрација.