

New thiocyanate-selective membrane electrodes based on a methyl methacrylate matrix

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A new simple procedure for the preparation of methyl methacrylate-based thiocyanate ion-selective membrane electrodes with an internal liquid contact is described. The electrodes consist of solid-state pellets, made from AgSCN or a mixture of Ag₂S/AgSCN in a methyl methacrylate matrix, made under pressure at an elevated temperature. The analytical behaviour of these electrodes is described in terms of potential-concentration curves, selectivity ratios, effect of pH, stability of the potential, response time and potentiometric titrations.

The discovery of the glass pH electrode can be considered the first step in the development of ion-selective electrodes. This electrode was succeeded by a new generation of ion-selective electrodes.

Ion-selective electrodes have undergone a remarkable development in the last 20 years. These electrochemical sensors have hitherto found numerous applications in direct potentiometry, potentiometric titrations, kinetics studies, biochemistry and biomedical research, industrial analytical control, *etc.*¹⁻⁴

In the field of ion-selective electrodes there have been only a few reports of solid-state thiocyanate-selective electrodes.⁵⁻¹⁵ Some of them indicate the possibility of preparing heterogeneous thiocyanate-selective electrodes based on polythene,^{10,11} graphite,¹³ silicone rubber¹⁴ or a natural oriental lacquer-Urushi¹⁵ as inert matrix.

This article describes a simple method for preparing thiocyanate-selective membrane electrodes based on a methyl methacrylate matrix. In addition, investigations of the mechanical and electrochemical properties of these electrodes are presented.

EXPERIMENTAL

Chemicals and solutions

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

Solutions of known concentrations (0.1 mol/dm³ AgNO₃, 0.1 mol/dm³ KSCN) were prepared by standard procedures.¹⁶ The ionic strength of the solution during the recording of the electrode calibration curves was maintained constant ($I = 0.1 \text{ mol/dm}^3$) by adding potassium nitrate.

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Preparation of membrane electrodes

The membrane electrodes were made of methacrylate resin Simgal (Galenika-Beograd): a) Simgal powder – methyl methacrylate polymer, benzoyl peroxide and inorganic pigments and b) Simgal liquid – methyl methacrylate monomer (polymerizes in the cold).

The silver salts (AgSCN , Ag_2S) used in the preparation of the membrane electrodes were prepared in our laboratory.

Silver thiocyanate, the active component of the membranes, was prepared as follows: a solution of silver nitrate (2.0 g AgNO_3 in 40 cm^3 double-distilled water) was added dropwise with constant stirring to a solution of potassium thiocyanate (1.0 g KNO_3 in 400 cm^3 double-distilled water). The precipitated silver thiocyanate was left to digest for 24 h after which it was filtered off, washed with double-distilled water until the filtrate gave no positive reaction on silver ions, dried at 105 °C, ground in an agate mortar and passed through a JEL, DIN No. 140E sieve.

Silver sulfide was prepared according to the procedure given by Camman and Rechnitz.¹⁷ After drying at 110 °C the precipitated silver sulfide was treated in the same manner as described for silver thiocyanate.

For the preparation of the electrode membranes, the required amounts of active components and Simgal powder were homogenized in a glass mortar. After adding the Simgal liquid, the mixture was again homogenized. The homogeneous mixture, without bubbles, was then carefully transferred into a stainless steel metal die placed on a glass plate. The inner diameter of the ring was 12.0 mm, and the heights were 0.5, 1.0, 2.0 and 3.0 mm, respectively. The upper surface of the thick mass was then pressed with a smooth metal rod (diameter 12.0 mm) in order to obtain a compact homogeneous mass. After polymerization at room temperature, the membrane obtained was heated at 110–130 °C, set in a press and pressed at 16 MPa over a period of 40–60 min, in order to obtain a more compact mass. Subsequently, the membrane obtained was polished first with alumina powder and then with Orion polishing strips. The prepared membranes were set into the respective bearing at the end of polyvinyl chloride tube of 15.0 cm length whose inner and outer diameters were 10.0 and 15.0 mm respectively (Fig. 1). The internal liquid contact was made by a silver wire in a solution of silver nitrate ($c = 1.0 \times 10^{-2} \text{ mol/dm}^3$). The electrodes were stored in a thiocyanate solution ($c = 1.0 \times 10^{-3} \text{ mol/dm}^3$) which was replaced with a freshly prepared solution every 10–15 days.

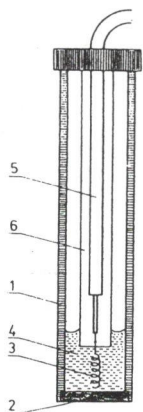


Fig. 1. Schematic view of a methyl methacrylate-based thiocyanate-selective electrode with a liquid internal contact: 1 – electrode body, 2 – membrane, 3 – silver wire, 4 – internal solution, 5 – connecting wire, 6 – plastic tubing.

Apparatus

The emf measurements were performed using an Orion Research digital ionanalyzer (Model 801A) and Radiometer saturated calomel electrode (Model K401) with a potassium nitrate salt bridge. An Elektrozveze Iskra-Kranj megaohmmeter (type MA 2070) was used for membrane resistance measurements. The temperature of the solutions was kept constant (25.0 ± 0.1 °C) with an MLW ultrathermostate (Model U-15-C). The solutions were stirred magnetically.

RESULTS AND DISCUSSION

Preliminary investigations involved testing known procedures for obtaining silver thiocyanate and silver sulfide in order to determine convenient conditions for their preparation. In addition, the conditions for the simple preparation of thiocyanate ion-selective membrane electrodes based on Simgal-methyl methacrylate resin were established.

Investigations showed that, with increasing membrane thickness the resistance of the electrodes increases and, in the case of membrane thicknesses greater than 1.5 mm, the electrode functions weakened. Because the 0.5 mm thick membranes do not have satisfactory mechanical stability, membranes with a thickness of 1.0 mm were prepared for further investigations.

When the content of the active components in the electrode membranes was larger than 70%, the potential of the electrodes prepared was found to depend on the concentration of thiocyanate in the solutions examined. Also, if the content of the methyl methacrylate resin was less than 15%, the membranes were mechanically unstable - after a short application (sometimes even on standing) they cracked.

On the basis of the results of these preliminary investigations, 28 electrodes with membranes containing 80-85% active components and 20-15% methacrylate resin were prepared: 8 electrodes contained membranes with incorporated silver thiocyanate (group I electrodes) and 20 electrodes contained membranes in which mixtures of silver thiocyanate and silver sulfide with mass ratios ranging from 3.25 : 1 to 1 : 3.25, were incorporated (group II electrodes).

The properties and the behaviour of the prepared electrodes were investigated over a period of more than 2 years.

It was found that the resistance of the group I electrodes varied from 2.5 - 10 M Ω , whereas that of the electrodes containing the same percentage of a mixture of silver thiocyanate and silver sulfide (group II electrodes) was 0.002 - 1.2 M Ω . The resistance of the group II electrodes having membranes with the same total percentage of active components was found to decrease with increasing amounts of the silver sulfide component.

Specific cell constant (obtained by extrapolation of $E/pSCN$ curve on $pSCN = 0$) of the electrodes prepared was positive: the potential of the group I electrodes was 121-135 mV and that of the group II electrodes was 109-204 mV.

The sensitivity, selectivity and other electrode functions of both electrode groups were similar. For group I and II electrodes, the lower limit of their Nernstian response was 1.0×10^{-5} to 6.0×10^{-6} mol/dm³ and 8.0×10^{-5} to 1.0×10^{-6} mol/dm³, and their detection limit² was 3.0×10^{-6} to 1.5×10^{-6} mol/dm³ and 1.5×10^{-6} to 3.0×10^{-7} mol/dm³, respectively. The slope of the calibration curves was 55.0 - 58.5 mV and 53.0 - 59.5 mV for the group I and II electrodes, respectively. The prepared electrodes retained their electrode function for a long time after their activation (Table I).

The response time of the electrodes was less than 2 min in 1.0×10^{-3} mol/dm³ 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 5 min.

TABLE I. Variations in the response ranges of methyl methacrylate-based thiocyanate-selective electrode with ageing

Nernstian limit (mol/dm ³) [*]	Detection limit (mol/dm ³) [*]	Specific cell constant (mV) ^x	Slope (mV/dec.conc)	Ageing [#] (days)
8.0×10^{-6}	2.0×10^{-6}	134.9	54.5	1
7.0×10^{-6}	3.5×10^{-6}	111.8	55.0	47
3.0×10^{-6}	8.0×10^{-7}	114.4	58.5	83
6.0×10^{-6}	1.5×10^{-6}	129.1	58.0	952

^{*} Terms are defined in Bailey ² pp. 50-52

^x Specific cell constant obtained by extrapolation of $E/pSCN^-$ curve on $pSCN^- = 0$

[#] Days after activation of the electrode

The previously mentioned data and the calibration curves of the prepared thiocyanate-selective electrodes (Fig. 2) show that they can be successfully applied to the determination of thiocyanate in solutions with concentrations up to 1.0×10^{-5} mol/dm³ using the direct potentiometric method.

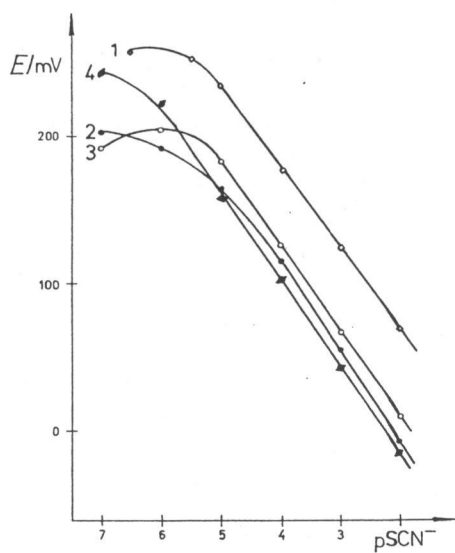


Fig. 2. Calibration curve of methyl methacrylate-based thiocyanate-selective electrodes with liquid internal contacts. Electrode membranes contained different amounts of silver thiocyanate and silver sulfide: 1) 35% AgSCN + 50% Ag₂S; 2) 20% AgSCN + 65% Ag₂S; 3) 65% AgSCN + 20% Ag₂S; 4) 42.5% AgSCN + 42.5% Ag₂S.

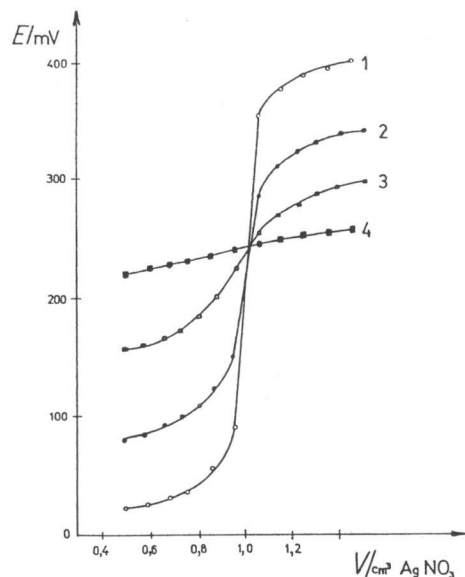


Fig. 3. Potentiometric titration curves for thiocyanate with silver nitrate solutions of different concentrations obtained with methyl methacrylate-based thiocyanate-selective electrode: (1) 1.0×10^{-2} mol/dm³ SCN⁻ + 1.0×10^{-1} mol/dm³ AgNO₃; (2) 1.0×10^{-3} mol/dm³ SCN⁻ + 1.0×10^{-2} mol/dm³ AgNO₃; (3) 1.0×10^{-4} mol/dm³ SCN⁻ + 1.0×10^{-3} mol/dm³ AgNO₃; (4) 1.0×10^{-5} mol/dm³ SCN⁻ + 1.0×10^{-4} mol/dm³ AgNO₃.

The effect of the pH on the electrode potential was investigated by following changes in the electrode potential with variation in the pH of the tested solutions (1.0×10^{-2} to 1.0×10^{-4} mol/dm³ thiocyanate, $I = 0.1$) caused by the addition of nitric acid or sodium hydroxide solution. The results obtained revealed that pH variations

do not affect the potential between pH 3 and 7, so that the electrodes can be safely used in this pH range for thiocyanate determination.

The electrodes also displayed a pronounced potential jump at the end point in potentiometric titrations of thiocyanate solutions with silver nitrate (Fig. 3). For example, it was found that the end points were in the vicinity of 266, 135 and 32 mV/0.05 cm³ of titrant for titrations of 1.0×10^{-2} , 1.0×10^{-3} and 1.0×10^{-4} mol/dm³ potassium thiocyanate solutions with 1.0×10^{-1} , 1.0×10^{-2} and 1.0×10^{-3} mol/dm³ silver nitrate solutions, respectively. These were potential changes of the electrode whose membrane contained a mixture of 42.5% silver thiocyanate and 42.5% silver sulfide in a methyl methacrylate matrix.

The selectivity coefficients of the electrodes, were determined by the direct and indirect potentiometric method¹ in the presence of chlorides, bromides, iodides, chromates, carbonates, arsenates, phosphates and hexacyanoferrate(II). The values obtained are given in Table II and they lie within the expected limits.

TABLE II. Selectivity coefficients of methyl methacrylate-based thiocyanate-selective electrode

Interfering ions	$K_{i,k}^a$	$K_{i,k}^b$
Cl ⁻	1.5×10^{-3}	5.2×10^{-3}
Br ⁻	2.0	-
I ⁻	100	-
CO ₃ ²⁻	2.3×10^{-5}	3.4×10^{-6}
CrO ₄ ²⁻	1.8×10^{-4}	1.1×10^{-5}
PO ₄ ³⁻	1.3×10^{-5}	1.3×10^{-7}
AsO ₄ ³⁻	3.6×10^{-4}	3.9×10^{-6}
[Fe(CN) ₆] ⁴⁻	6.3×10^{-4}	-

^a $K_{i,k}$ values measured directly

^b $K_{i,k}$ values measured indirectly

ИЗВОД

НОВЕ ТИОЦИЈАНАТНЕ СЕЛЕКТИВНЕ МЕМБРАНСКЕ ЕЛЕКТРОДЕ НА БАЗИ МЕТИЛ МЕТАКРИЛАТНЕ МАТРИЦЕ

КРУМЕ КАЛАЈЦИЈЕВСКИ и ВЕРА ТРАЈКОВСКА

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Описан је нови, једноставни поступак за припремање тиоцијанатних јон-селективних мембранских електрода, са унутрашњим течним контактом, на бази метил метакрилатне матрице. Електроде садрже чврсте мембране, направљене из AgSCN или смеше Ag₂S/AgSCN у метил метакрилатној матрици, применом пресовања на датој температури. Аналитичке карактеристике ових електрода описани су кривама потенцијал-концентрација, коефицијентом селективности, ефектом рН, стабилности потенцијала, временом одговора и потенциометријском титрацијом.

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