

## **Preparation of a new type of chloride-selective electrode based on a methyl methacrylate matrix. Its properties and application**

TIBOR J. PASTOR, MILKA M. PASTOR and KRUME KALAJDŽIEVSKI\*

*Department of Chemistry, Faculty of Science, University of Belgrade, P. O. Box 550, YU-11001 Belgrade, Yugoslavia and \*Department of Chemistry, Faculty of Sciences, University of Skopje, YU-91000, Yugoslavia*

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Methyl methacrylate-based chloride ion-selective membrane electrodes with an internal solid contact were prepared. The stability, detection limits, slope of the calibration curves, standard potential and the selectivity of the prepared electrodes were found to be satisfactory. The new electrodes can be successfully applied to the determination of chlorine in organic and biologically active substances by the direct potentiometry and potentiometric titration after their combustion in an oxygen atmosphere.

Recently the number of precipitate-based ion-selective electrodes has significantly increased.<sup>1-5</sup> These electrodes were made in various forms and the main points of variation among the electrodes of the same kind involved the construction of the membrane and the internal contact to the membrane. Homogeneous membranes consisted entirely of an active material, whereas heterogeneous membranes consisted of an active material supported in an inert matrix such as silicone rubber, PVC or polythene. Data have also been published on the preparation of heterogeneous ion-selective electrodes based on methacrylates as inert matrix by molding mixtures of insoluble precipitates with thermoplastic polymers at suitable temperatures and pressures,<sup>6-8</sup> or by evaporating the solvent (tetrahydrofuran) after placing the investigated solution for membrane preparation into the respective glass casting ring, resting on a sheet of plate glass.<sup>9,10</sup> The membranes of methyl methacrylate-based iodide-selective<sup>11</sup> and bromide-selective<sup>12</sup> electrodes were prepared by the polymerization of methyl methacrylate monomer after placing a homogenized mixture containing known ratios of the active components and methyl methacrylate monomer and polymer into a metal die with corresponding dimensions.

This paper is aimed at establishing conditions for the preparation of heterogeneous methyl methacrylate-based chloride ion-selective electrodes by the polymeri-

zation of methyl methacrylate monomer. The mechanical and electrochemical properties of the prepared electrodes and their possible application in the analysis of organic and biologically active substances were also investigated.

## EXPERIMENTAL

### *Chemicals and solutions*

All chemicals used were of analytical reagent-grade (Merck). Stock solutions were prepared by standard procedures.<sup>13,14</sup> Sodium chloride solutions (Orion, 94-17-06) were also used. The ionic strength of solutions during the recording of the electrode calibration curves as well as in direct potentiometric determinations was maintained constant ( $I = 0.1$ ) by adding potassium nitrate.

### *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; b) Simgal liquid — methyl methacrylate monomer (polymerizes when cold), and a tertiary amine, produced from Howmedica International LTD, London, crude materials.

Silver chloride, the active component of the membranes, was prepared by adding dropwise a solution of silver nitrate (2.46 g) in double distilled water (40 cm<sup>3</sup>) to a solution of potassium chloride (0.90 g) in double distilled water (400 cm<sup>3</sup>) acidified with nitric acid (0.05 mol/dm<sup>3</sup>), with constant stirring of the reaction mixtures. The precipitated silver chloride was left to digest for 24 h, after which it was filtered off and washed with double distilled water until the filtrate gave no positive reaction for silver ions. The precipitate was dried at 105 °C, ground in an agate mortar, and passed through a JEL, DIN No. 105E sieve. The particle diameter was less than 0.038 mm.

Silver sulfide was prepared according to the procedure given by Camman and Rechnitz.<sup>15</sup> After drying at 110 °C, the precipitated silver sulfide was treated in the same manner as described for silver chloride.

For the preparation of the electrode membranes, the required amounts of active components and Simgal powder were homogenized in a glass mortar, Simgal liquid was added and the mixture was again homogenized. The homogeneous mixture without bubbles was then transferred into a stainless steel metal die placed on a glass plate. The inner diameter of the ring was 11.0 mm and the heights were 0.5, 1.0, 1.5 and 2.0 mm, respectively. The upper surface of the thick mass was then pressed with a smooth metal rod (diameter, 11.0 mm) in order to obtain a compact homogeneous mass. After the polymerization at room temperature was over, the membrane obtained was polished, first with a fine-grain Podravka-Bellupo polishing strip and then with Orion polishing strips (94-82-01).

The membranes prepared were set into the respective bearing at the end of a polyvinyl chloride tube of 15 cm length whose inner and outer diameter was 9.0 and 14.0 mm respectively; they were stuck with the mixture used for their preparation. The internal solid contact was made by fixing silver wire to the membrane of the electrodes with the mixture used for the preparation of membranes (Fig. 1).

The electrodes either were stored in a  $1.0 \times 10^{-3}$  mol/dm<sup>3</sup> potassium chloride solution which was replaced every 10—15 days with a freshly prepared solution, or were kept in dry air with a protective cap. After use, the electrodes were rinsed with double distilled water and blot dried.

### *Apparatus*

The measurements were performed using an Orion Research digital ionanalyzer (Model 801A), a Radiometer PHM 26 pH-millivoltmeter equipped with a recorder, and an Elektrovezve megaohmmeter (type 2070). The temperature of the magnetically stirred solutions was kept constant ( $25.0 \pm 0.1$  °C) with an ultrathermostat (Model U-15-C). A commercial Orion chloride electrode (Model 94—17A), an Orion double-junction reference electrode (Model 90—02), and a Radiometer saturated calomel electrode (Model K 401) were used.

The combustion of substances in an oxygen atmosphere was carried out in 300 or 500 cm<sup>3</sup> vessels. The combustion products were dissolved in 10.0 cm<sup>3</sup> 1.0 mol/dm<sup>3</sup> potassium hydroxide to which four drops of hydrogen peroxide (30%) were added. Prior to the determination of chloride the solution being examined was neutralized and made slightly acidic with dilute nitric acid.

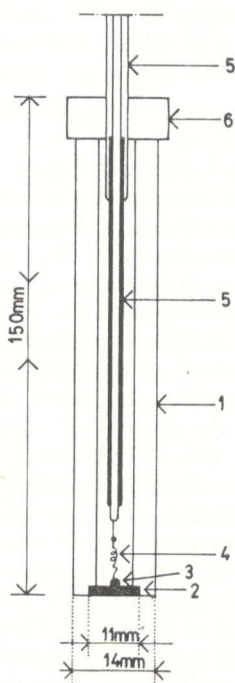


Fig. 1. Schematic of a methyl methacrylate-based chloride-selective electrode with a solid internal contact: 1) electrode body, 2) membrane, 3) solid contact, 4) silver wire, 5) connecting wire, and 6) electrode cap.

## RESULTS AND DISCUSSION

The preparation of the active components for chloride ion-selective membrane electrodes was first investigated. To this aim the procedures described in the literature for the synthesis of AgCl and Ag<sub>2</sub>S were checked and modified. In parallel, according to experience gained earlier,<sup>12</sup> electrode membranes of various composition and thickness based on methacrylate resin (Simgal, Galenika — Beograd) were prepared by the polymerization of methyl methacrylate monomer at room temperature and under atmospheric pressure.

The characteristics of the prepared electrodes showed that with increasing membrane thickness, the resistance of the electrodes increased and in the case of membrane thickness greater than 1.5 mm, their electrode functions were weakened; the mechanical stability of electrodes with a membrane thickness up to 0.7 mm was found to be small. Because of that, membranes with a thickness of 1.0 mm were prepared for further investigations. By changing the membrane composition it was established that the potential of the prepared electrodes depended on the concentration of chloride ions in the solutions examined only when the content of the active components in the electrode membranes was larger than 70%. When the amount of methacrylates in the membranes exceeded 30%, the resistance of the electrodes was large, but when the membranes contained only 10% matrix,

they were mechanically unstable (for example, fissures were found in electrode membranes containing 70% AgCl, 20% Ag<sub>2</sub>S and 10% methyl methacrylate, already 13–20 days after their application).

On the basis of the results of preliminary investigations, 35 electrodes were prepared with a membrane thickness of 1.0 mm, containing 70–90% active components and 30–10% methyl methacrylate resin: 10 electrodes contained membranes with incorporated silver chloride and 25 electrodes contained membranes in which mixtures of silver chloride and silver sulfide in a ratio ranging from 1:5 to 5:1, were incorporated.

The properties and the behaviour of the prepared electrodes were investigated over a period of 2 years. It was found that the resistance of the electrodes whose membranes contained 80–87% silver chloride (electrodes of group I) ranged from 170 to 155 MΩ, whereas that of the electrodes containing the same percentage of a mixture of silver chloride and silver sulfide (electrodes of group II) was 120 to 0.9 MΩ. The resistance of the group II electrodes with the same total percentage of active components in their membranes was found to decrease with increasing amounts of silver sulfide. The standard potential of the prepared electrodes was positive (230–295 mV). The sensitivity, selectivity and other electrode functions of both electrode groups were the best when the content of active components in their membranes was approximately 85% (84–86%). For group II electrodes it was very important that the ratio of silver chloride to silver sulfide in their membranes was from 1:1 to 1:1.5. The lower limit of their Nernstian response was  $4.0 \times 10^{-4}$  to  $2.0 \times 10^{-4}$  mol/dm<sup>3</sup>, and their detection limit<sup>1,16</sup>  $4.0 \times 10^{-5}$  to  $1.0 \times 10^{-5}$  mol/dm<sup>3</sup>; the slope of the calibration curves, even after longer application of the electrodes, was close to the theoretical one (57–61 mV). The effect of the pH of the examined solutions ( $1.0 \times 10^{-2}$  to  $1.0 \times 10^{-3}$  mol/dm<sup>3</sup>,  $I = 0.1$ ) on the electrode potential was investigated by following potential variations with pH changes on the addition of nitric acid and/or sodium hydroxide solution. The results obtained revealed that the pH change did not affect the potential within pH 3–10. The response time of the electrodes was better than 15 s in  $1.0 \times 10^{-2}$  mol/dm<sup>3</sup> chloride solutions as well as in solutions of higher chloride concentrations; in  $1.0 \times 10^{-4}$  mol/dm<sup>3</sup> chloride solutions the response time was longer but did not exceed 1 min. The characteristics of methyl methacrylate-based chloride ion-selective electrodes were close to those of the Orion chloride electrode Model 94–17 A (Table I). The selectivity coefficients of the electrodes were determined by direct potentiometric methods or indirect potentiometric methods<sup>2</sup> in the presence of carbonates, phosphates, chromates and arsenates, respectively. The values obtained were within the corresponding values of the Orion chloride electrode Model 94–17A (Table II).

### *Analytical application*

The previously mentioned data and the calibration curves of chloride ion-selective electrodes with a methyl methacrylate matrix (Fig. 2) show that they can be successfully applied to the determination of chloride concentrations up to  $2.0 \times 10^{-4}$  mol/dm<sup>3</sup> using the direct potentiometric method. They also show a pronounced potential jump at the end point in potentiometric titrations of chloride solutions with silver nitrate. For example, it was found that the potential changes of the electrodes whose membranes contained 42.5% silver chloride and 42.5% silver sul-

TABLE I. Variations in the response ranges of chloride-selective electrodes with ageing

Methyl methacrylate-based chloride-selective electrode					Orion 94—17A chloride electrode				
Nernstian limit <sup>a</sup> (mol/dm <sup>3</sup> )	Detection limit <sup>a</sup> (mol/dm <sup>3</sup> )	Standard potential (mV)	Slope (mV/dec. conc.)	Ageing <sup>b</sup> (days)	Nernstian limit <sup>a</sup> (mol/dm <sup>3</sup> )	Detection limit <sup>a</sup> (mol/dm <sup>3</sup> )	Standard potential (mV)	Slope (mV/dec. conc.)	Ageing <sup>b</sup> (days)
$2.6 \times 10^{-4}$	$3.0 \times 10^{-5}$	239.0	61.0	4	$3.0 \times 10^{-4}$	$2.0 \times 10^{-5}$	242.0	58.0	1
$2.0 \times 10^{-4}$	$2.0 \times 10^{-5}$	239.0	61.0	50	$2.0 \times 10^{-4}$	$2.0 \times 10^{-5}$	235.0	60.0	280
$4.0 \times 10^{-4}$	$2.7 \times 10^{-5}$	244.0	60.0	120	$2.2 \times 10^{-4}$	$2.6 \times 10^{-5}$	236.0	60.0	420
$2.7 \times 10^{-4}$	$2.9 \times 10^{-5}$	243.0	59.0	430	$3.5 \times 10^{-4}$	$4.0 \times 10^{-5}$	242.0	60.0	573
$3.0 \times 10^{-4}$	$2.5 \times 10^{-5}$	246.0	57.0	587	$5.0 \times 10^{-4}$	$6.0 \times 10^{-5}$	240.0	58.0	763

<sup>a</sup> Terms are defined in Ref. 1, pp. 50—52

<sup>b</sup> Days after activation of the electrode

fide, in the titration of  $1.0 \times 10^{-2}$  mol/dm<sup>3</sup> chloride solution with  $1.0 \times 10^{-3}$  silver nitrate solution were about 100 mV/0.4 cm<sup>3</sup> of the titrant. Possible applications of chloride ion-selective electrodes prepared with methyl methacrylate resin were shown by determining the chlorine content in organic and biologically active substances, after their combustion in oxygen atmosphere by the modified Schöniger

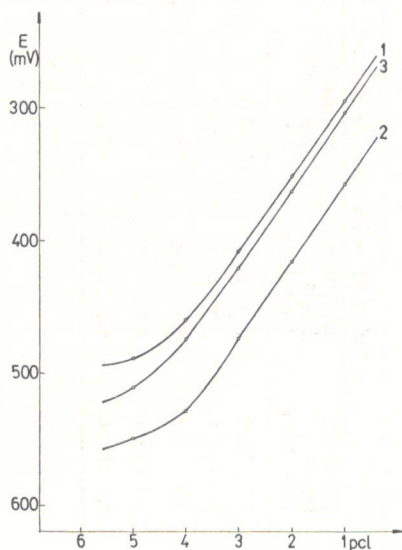


Fig. 2. Calibration curve of methyl methacrylate-based chloride ion-selective electrodes whose membranes contain: 1) 35% AgCl + 50% Ag<sub>2</sub>S and 2) 42.5% AgCl + 42.5% Ag<sub>2</sub>S; 3) calibration curve of Orion chloride electrode Model 94—17A.

TABLE II. Selectivity coefficients of chloride-selective electrodes

Interfering ions	Methyl methacrylate-based chloride-selective electrode		Orion '94—17A chloride electrode	
	$K_{ik}^a$	$K_{ik}^b$	$K_{ik}^a$	$K_{ik}^b$
CO <sub>3</sub> <sup>2-</sup>	$8.1 \times 10^{-5}$		$7.9 \times 10^{-5}$	
PO <sub>4</sub> <sup>3-</sup>	$1.6 \times 10^{-4}$	$2.3 \times 10^{-4}$	$3.0 \times 10^{-4}$	$1.9 \times 10^{-4}$
CrO <sub>4</sub> <sup>2-</sup>		$8.8 \times 10^{-5}$		$5.8 \times 10^{-5}$
AsO <sub>4</sub> <sup>3-</sup>		$6.8 \times 10^{-4}$		$4.7 \times 10^{-4}$

<sup>a</sup> $K_{ik}$  values measured by direct method

<sup>b</sup> $K_{ik}$  values measured by indirect method

procedure. The determinations were carried out by direct potentiometry and potentiometric titrations. The results obtained are given in Table III. They are sufficiently accurate and reproducible.

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TABLE III. Comparison of results obtained for chloride content by different techniques with a methyl methacrylate-based chloride-selective electrode

Substance	Actual chlorine content (%)	Taken (mg)	No. of dets.	Potentiometric titration		Direct potentiometry	
				Found <sup>a</sup> (%)	Recovery <sup>a</sup> (%)	Found <sup>a</sup> (%)	Recovery <sup>a</sup> (%)
Diazepam	12.45	31.1	6	12.4±0.2	99.6±0.2	12.3±0.5	98.8±0.5
Dimenhydrinate	7.54	51.8	5	7.5±0.2	99.5±0.2	7.6±0.7	100.8±0.7
Chlordiazepoxide	11.83	22.3	6	11.9±0.5	100.6±0.5	11.9±0.4	100.6±0.4
Chloramphenicol	21.95	17.8	6	21.6±0.2	98.4±0.2	21.6±0.4	98.4±0.4
Chloramphenicol palmitate	12.63	29.5	5	12.4±0.3	98.2±0.3	12.4±0.2	98.2±0.2

<sup>a</sup> Mean ± standard deviation

## ИЗВОД

ИЗРАДА НОВОГ ТИПА ХЛОРИД-СЕЛЕКТИВНИХ ЕЛЕКТРОДА НА БАЗИ  
МЕТИЛМЕТАКРИЛАТА — ЊИХОВЕ ОСОБИНЕ И ПРИМЕНА

Т. Ј. ПАСТОР, М. М. ПАСТОР и КРУМЕ КАЛАЈЦИЕВСКИ\*

Хемијски факултет, Природно-мајематички факултет, Универзитет у Београду, б. бр. 550, 11001 Београд и  
\*Хемијски институт, Природно-мајематички факултет, Универзитет у Скопју, 91000 Скопје

Израђене су хлорид-селективне електроде на бази метилметакрилата са унутрашњим чврстим контактом. Стабилност, нагиб калибрационих кривих, стандардни потенцијал и селективност припремљених електрода су задовољавајуће. Оне се могу успешно применити за одређивање хлора у органским и биолошки активним супстанцама директном потенциометријском методом и потенциометријском титрацијом након њиховог сагоревања у атмосфери кисеоника.

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