

New Bromide-Selective Membrane Electrodes Based on a Methyl Methacrylate Matrix and Their Use in Drug Analysis

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ABSTRACT

A new, simple procedure for the preparation of methyl methacrylate-based bromide ion-selective membrane electrodes with an internal solid contact is described. The stability, response range, and slope as well as the selectivity and interference-free pH range of these electrodes were found to be satisfactory. The electrodes were applied to the determination of low bromine levels in biologically active substances with direct potentiometry and potentiometric titration after their combustion in an oxygen atmosphere. The results obtained are accurate and reproducible.

INTRODUCTION

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. In the 1960s, Pungor *et al.* prepared precipitate-based, ion-selective electrodes with membranes consisting of silver salts dispersed in paraffin [1] or in silicone rubber [2–10]. The latter progress was soon followed by the construction of the LaF₃-type fluoride-selective electrode [8, 11] as well as silver and halide electrodes with membranes consisting of pressed pellets of the appropriate silver salt coprecipitated with silver sulfide [5, 8]. Data were published on the preparation of heterogeneous ion-selective electrodes based on inert organic polymer matrixes (methacrylic esters and polythene) by molding mixtures of insoluble precipitates with thermoplastic polymers at suitable temperatures and pressures [12–14]. The properties of divalent ion-selective electrodes based on polyvinyl chloride and polymethyl acrylate matrix membranes have also been investigated [15, 16]; the latter were obtained by evaporating the solvent (tetrahydrofuran) after placing the investigated solution preparation into the respective glass casting ring (resting on a sheet of plate glass).

This article describes a simple method for preparing methyl methacrylate-based bromide-selective membrane electrodes with an internal silver contact. The electrode membranes were prepared by the polymerization of

methyl methacrylate monomer after placing a homogenized mixture containing known ratios of the active component and methyl methacrylate monomer and polymer into a metal die with corresponding dimensions. In addition, investigations of the mechanical and electrochemical properties of these electrodes and their possible application to the analysis of biologically active bromine compounds are presented.

EXPERIMENTAL

Chemicals and Solutions

Analytical reagent grade chemicals (Merck) were used without further purification. Solutions of known concentrations were prepared by standard procedures [17, 18]. Solutions of sodium bromide (Orion, 94-35-06) and sodium chloride (Orion, 94-17-06) were also used. The ionic strength of the solution 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): (1) Simgal powder—methyl methacrylate polymer, benzoyl peroxide, and inorganic pigments; (2) Simgal liquid—methyl methacrylate monomer (polymerizes when cold), and the tertiary amine produced by Howmedica International, Ltd., London, and crude materials.

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Silver bromide, the active component of the membranes, was prepared as follows. A solution of silver nitrate (3.42 g) in double-distilled water (40 cm³) was added dropwise with constant stirring to a solution of potassium bromide (2.00 g) in double-distilled water (400 cm³) acidified with nitric acid (0.005 mol/dm³). The precipitated silver bromide was left to digest for 24 hours, after 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 No. 150E sieve. The particle diameter was less than 0.038 mm.

Silver sulfide was prepared according to the procedure given by Camman and Rechnitz [19]. After drying at 110°C, the precipitated silver sulfide was treated in the same manner as described for silver bromide.

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 11.0 mm, and the heights were 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 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 polymerization at room temperature, the membrane obtained was polished, first with a fine-grain Podravka-Belupo polishing strip and then with Orion polishing strips (94-82-01).

The prepared membranes were set into the respective bearing at the end of a 15 cm long polyvinyl chloride tube (inner and outer diameters, 9.0 and 14.0 mm, respectively) and fixed by means of the mixture used for their preparation. The internal solid contact was made by fixing a silver wire to the electrode membranes with the mixture used for their preparation (Figure 1).

The electrodes either were stored in a 1.0×10^{-3} mol/dm³ bromide solution, which was replaced with a freshly prepared solution every 10–15 days or were kept in dry air with a protective cap. After use, the electrodes were rinsed with 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 Elektrozveze megaohmmeter (type 2070). The temperature of the magnetically stirred solutions was kept constant ($25.0 \pm 0.1^\circ\text{C}$) with an MLW ultrathermostat (Model U-15-C). A commercial Orion bromide electrode (Model 94-35A), 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 cm³ vessels made according to Sokolova *et al.* [20]. The combustion products were dissolved in 10.0 cm³ 1.0 mol/dm³ potassium

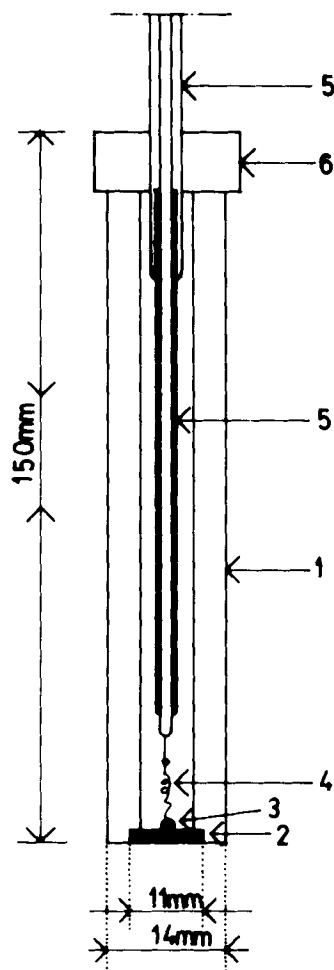


FIGURE 1. Schematic of a methyl methacrylate-based bromide-selective electrode with a solid internal contact. (1) Electrode body; (2) membrane; (3) solid contact; (4) silver wire; (5) connecting wire; (6) electrode cap.

hydroxide to which four drops of hydrogen peroxide (30%) were added. Prior to the determination of bromide, the solution being examined was neutralized and made slightly acidic with dilute nitric acid.

RESULTS AND DISCUSSION

Preliminary investigations involved testing known procedures for obtaining of silver bromide and silver sulfide in order to discover convenient conditions for their preparation. In addition, conditions for the simple preparation of bromide ion-selective membrane electrodes based on methyl methacrylate resin (Simgal, Galenika, Beograd) at room temperature and under atmospheric pressure were established.

Investigations have shown 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 were weakened. Because

TABLE 1 Variations in the Response Ranges of Bromide-Selective Electrodes with Aging

<i>Methyl Methacrylate-Based Bromide-Selective Electrode</i>					<i>Orion 94-35A Bromide Electrode</i>				
<i>Nernstian Limit</i> (mol/dm ³) ^a	<i>Detection Limit</i> (mol/dm ³) ^a	<i>Standard Potential</i> (mV)	<i>Slope</i> (mV/Dec. Conc.)	<i>Aging</i> ^b (Days)	<i>Nernstian Limit</i> (mol/dm ³) ^a	<i>Detection Limit</i> (mol/dm ³) ^a	<i>Standard Potential</i> (mV)	<i>Slope</i> (mV/Dec. Conc.)	<i>Aging</i> ^b (Days)
4.0×10^{-5}	4.5×10^{-6}	119.0	57.0	4	6.0×10^{-6}	1.0×10^{-6}	95.5	60.0	3
3.0×10^{-5}	4.5×10^{-6}	117.0	58.0	19	6.0×10^{-6}	1.0×10^{-6}	82.0	60.0	74
2.5×10^{-5}	1.5×10^{-6}	101.0	59.0	42	6.0×10^{-6}	1.0×10^{-6}	80.0	61.0	109
2.3×10^{-5}	3.8×10^{-6}	90.0	60.5	156	1.5×10^{-5}	1.0×10^{-6}	86.5	61.5	138
3.5×10^{-5}	2.6×10^{-6}	92.0	60.0	380	9.6×10^{-6}	2.1×10^{-6}	84.0	60.5	340
4.2×10^{-5}	3.5×10^{-6}	95.0	59.5	653	2.0×10^{-5}	3.5×10^{-6}	88.0	59.5	628

^a Terms are defined in Bailey [5], pp. 50–52.
^b Days after activation of the electrode.

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 active components in the electrode membranes was larger than 70%, the potential of the electrodes prepared was found to depend on the concentration of bromide in the solutions examined. If the amount of methacrylates in the membranes exceeds 30%, the resistance of the electrodes is large (5,000 M Ω), but if the content of methacrylate is less than 15% the membranes are mechanically unstable—after a short application, sometimes even on standing, they crack. For example, fissures were found in the electrode membranes containing 10% methacrylate resin after 20–30 days.

On the basis of the results of preliminary investigations, 40 electrodes with membranes containing 70–90% active components and 30–10% methacrylate resin were prepared: 15 electrodes contained membranes with incorporated silver bromide and 25 electrodes contained membranes in which mixtures of silver bromide and silver sulfide in a ratio ranging from 7.5:1 to 1:7.5 were incorporated.

The properties and the behavior of the prepared electrodes were investigated over a period of more than 2 years. It was found that the resistance of the electrodes whose membranes contained 70–85% potassium bro-

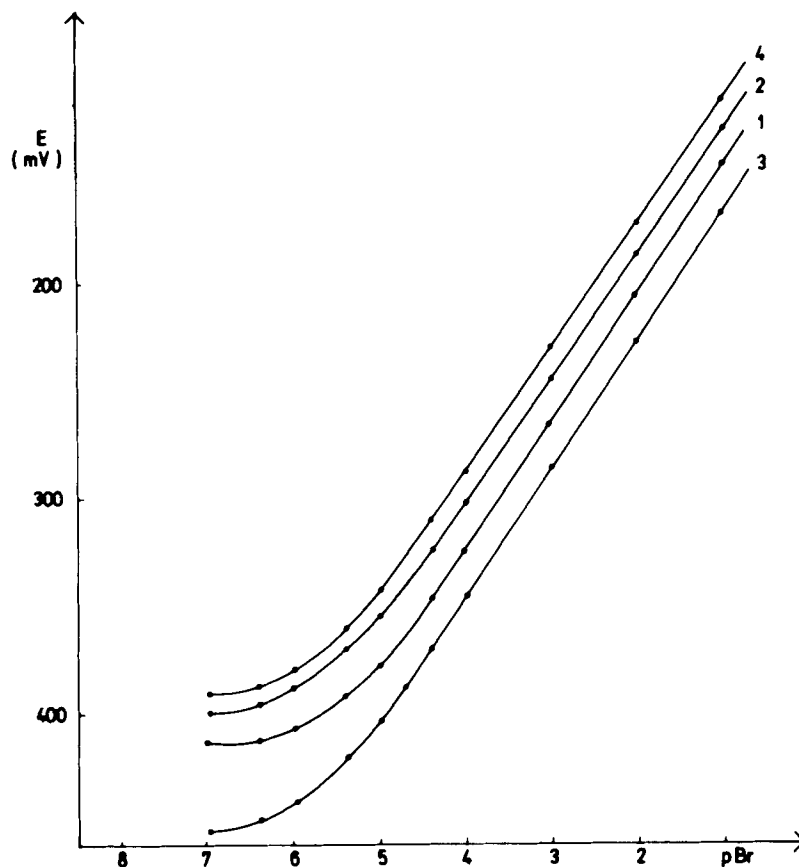
midate (electrodes of group I) varied from 150 to 30 M Ω , whereas that of the electrodes containing the same percentage of a mixture of silver bromide and silver sulfide (electrodes of group II) was 90–0.5 M Ω . The resistance of the group II electrodes having membranes with the same total percentage of active components was found to decrease with increasing amounts of the silver sulfide component. The standard potential of the electrodes prepared was positive: the potential of the group I electrodes was 70–100 mV and that of the group II electrodes was 80–180 mV. The sensitivity, the selectivity, and other electrode functions of both electrode groups were similar, but they displayed the best properties when the content of active components in their membranes was 80–85%. For group II electrodes, it is very important that the ratio of silver bromide to silver sulfide in their membranes be between 3:1 and 1:3. The lower limit of their Nernstian response was 8.0×10^{-5} to 1.0×10^{-5} mol/dm³, and their detection limit [5, 21] was 5.0×10^{-6} to 1.5×10^{-6} mol/dm³. The slope of the calibration curves, even after a longer application, was close to theoretical (58–61 mV). The response time of the electrodes was better than 20 seconds in 1.0×10^{-3} mol/dm³ bromide solutions as well as in solutions with higher bromide concentrations. In 1.0×10^{-4} mol/dm³ bromide solutions, however, the response time was not as rapid, but it did not exceed

TABLE 2 Selectivity Coefficients of Bromide-Selective Electrodes

<i>Interfering Ions</i>	<i>Methyl Methacrylate-Based Bromide-Selective Electrode</i>		<i>Orion 94-35A Bromide Electrode</i>	
	K_{ij}^a	K_{ij}^b	K_{ij}^a	K_{ij}^b
Cl ⁻	3.2×10^{-3}	5.5×10^{-3}	3.0×10^{-3}	4.0×10^{-3}
CrO ₄ ²⁻		3.5×10^{-7}		2.5×10^{-7}
PO ₄ ³⁻	4.3×10^{-6}	6.5×10^{-7}	6.3×10^{-6}	4.5×10^{-7}
AsO ₄ ³⁻		3.3×10^{-6}		3.5×10^{-6}
CO ₃ ²⁻		4.0×10^{-7}		3.0×10^{-7}

^a K_{ij} values measured directly.
^b K_{ij} values measured indirectly.

FIGURE 2. Calibration curve of methyl methacrylate-based bromide selective electrodes with solid internal contacts. Electrode membranes contain different amounts of silver bromide and silver sulfide: (1) 20% AgBr + 65% Ag₂S; (2) 35% AgBr + 50% Ag₂S; (3) 42.5% AgBr + 42.5% Ag₂S; (4) 70% AgBr + 15% Ag₂S.



1 minute. The characteristics of the methacrylate-based bromide-selective electrodes were close to those of the Orion bromide electrode Model 94-35A (Table 1). The selectivity coefficients of the electrodes were determined by direct and indirect potentiometric methods [4] in the presence of chlorides, chromates, carbonates, arsenates, and phosphates, respectively. The values obtained were within the expected limits and were in agreement with those of the Orion bromide electrode Model 94-35A (Table 2).

Analytical Application. The previously mentioned data and the calibration curves of ion-selective electrodes prepared with methyl methacrylate (Figure 2) show that

they can be successfully applied to the determination of bromide in solutions with concentrations up to 1.0×10^{-5} mol/dm³ using the direct potentiometric method. The effect of the pH on the electrode potential was investigated by following changes in the electrode potential with variations in the pH change of tested solutions (1.0×10^{-2} to 1.0×10^{-4} mol/dm³ bromide, $I = 0.1$) caused by the addition of nitric acid and/or sodium hydroxide solution. The results obtained revealed that pH variations do not affect the potential between pH 3 and 11, so that the electrodes can be safely used in this pH range for bromide determination. The electrodes also displayed a pronounced potential jump at the end point in potentiometric titrations of bromide solutions with silver nitrate

TABLE 3 Comparison of Results Obtained for Bromine Content by Different Techniques with a Methyl Methacrylate-Based Bromide-Selective Electrode

Substance	Actual Bromine Content (%)	Taken (mg)	Number of Detections	Potentiometric Titration ^a		Direct Potentiometry ^a	
				Found (%)	Recovery (%)	Found (%)	Recovery (%)
Bromazepam	25.28	31.3	10	25.1 ± 0.4	99.3 ± 0.4	24.9 ± 0.4	98.5 ± 0.4
Pro-Banthine	17.82	41.0	5	17.6 ± 0.8	98.8 ± 0.8	17.6 ± 0.7	98.8 ± 0.7
Bronopol	39.95	20.6	6	39.3 ± 0.4	98.5 ± 0.4	39.6 ± 0.3	99.1 ± 0.1

^a Mean plus or minus the standard deviation.

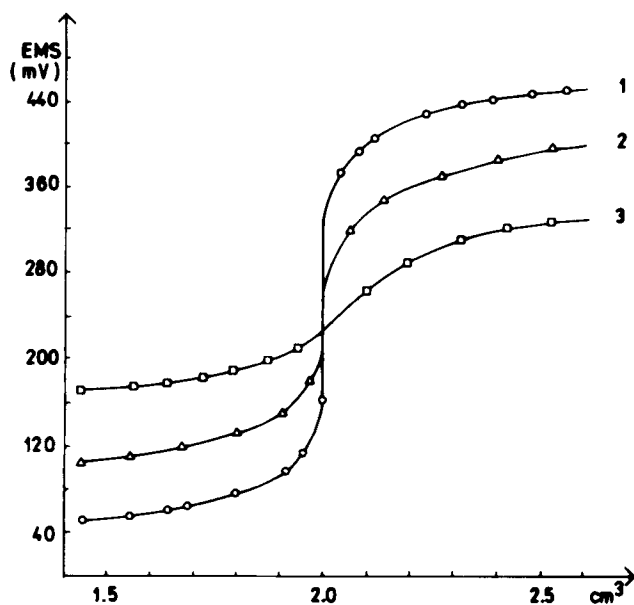


FIGURE 3. Potentiometric titration curves for bromide with silver nitrate solutions of different concentrations obtained with the methyl methacrylate-based bromide-selective electrode: (1) 1.0×10^{-2} mol/dm³ Br⁻ + 1.0×10^{-1} mol/dm³ AgNO₃ (2) 1.0×10^{-3} mol/dm³ Br⁻ + 1.0×10^{-2} mol/dm³ AgNO₃ (3)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

(Figure 3). For example, it was found that potential changes of the electrode whose membrane contained a mixture of 35% of silver bromide and 50% of silver sulfide in the vicinity of the end point were 228, 102, and 16 mV/0.04 cm³ of the titrant in titrations of 1.0×10^{-2} , 1.0×10^{-3} , and 1.0×10^{-4} mol/dm³ potassium bromide solutions with 1.0×10^{-1} , 1.0×10^{-2} , and 1.0×10^{-3} mol/dm³ silver nitrate solutions, respectively. The possibility of applying the electrodes prepared in this way to analytical determinations has been shown by determining the bromine content in organic and biologically active substances after their combustion in oxygen flask. The bromine content of such substances was determined by direct potentiometry and potentiometric titrations. The

results obtained, which are given in Table 3, indicate good accuracy and reproducibility.

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