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A Silver/Silver Sulfide Selective Micro-Electrode Prepared by Chemical Treatment of Silver Wire

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The preparation conditions and the performance of a small size Ag/Ag_2S selective electrode are described. The analytical behaviour of this electrode, made by chemical treatment of a silver wire, is described in terms of potential — concentration curves, standard potential, lifetime and electrode selectivity. A series of electrodes have been prepared and investigated. Their response and selectivity to Ag^+ and S^{2-} are measured and compared with those of a commercial Orion silver/sulfide electrode. Several titrations were performed to evaluate the performances of the electrode. The investigated electrode can be used, as a good substitute for the commercial silver/sulfide electrode, in a wide variety of practical analytical systems.

INTRODUCTION

The silver sulfide ion-selective electrode can be produced in various versions[1]. In recent years, solid-state silver sulfide membrane electrodes selective towards Ag^+, S^{2-}, as well as other species forming complexes with the membrane materials, have been used for a variety of analytical applications[2-12]. Also, silver/silver sulfide electrodes can be prepared by anodic polarization of a silver rod in a pure solution of sodium sulfide. They are sensitive to sulfide and to silver(I) ions[13,14]. These electrodes were used as indicator sensors in potentiometric titrations, but not quantitatively compared to the silver sulfide membrane electrode. As be noted[15], a silver/silver sulfide electrode can be prepared by dipping the platinum spiral, coated with porous silver by thermal decomposition of silver oxide paste, into an aqueous solution of hydrogen sulfide. The stannous sulfide based sulfide responsive ion selective electrode, as a novel solid-state mebrane electrode, was prepared by electrolyzing tin onto a platinum wire, followed by soaking the treated wire in a saturated hydrogen sulfide solution (16). The response of sulfide is linear in both aqueous and aqueous-alcoholic media. Recently, different metal-metal sulfide electrodes have been prepared in the similar manner[17]. Such electrodes are prepared by electro-depositing the appropriate element (As, Mo, Sb) on platinum wires and then immersing the wires overnight in saturated aqueous H_2S.

Although chemically and electrochemically prepared Ag/Ag_2S electrodes were reasonably well behaved at electromotive force measurements[15,18], the analytical examination has not been extended.

This paper reports on an investigation of the preparation conditions and the performance of a simple small size Ag/Ag_2S selective electrode made by chemical treatment of a silver wire. The electrode is selective to silver and sulfide ions and showed an essentially identical response when compared side-by-side with a commercial silver/sulfide electrode, in experiments characteristic for of this kind of electrodes. The cost of this electrode is very low in comparison with the commercially available electrodes.

EXPERIMENTAL

Reagents

All chemicals used in this study were of analytical grade and were used without further purification. Calibration solutions were prepared from silver nitrate (for silver ion) and sodium sulfide nonahydrate (for sulfide ion). Also, the stock and standard sulfide solutions were prepared with SAOB-II[19] or 1.0 mol dm^{-3} sodium hydroxide containing ascorbic acid (20 mg cm^{-3}). All solutions were prepared with deionized water and the water for sulfide ion solutions was deaerated with argon. The concentration of sodium sulfide solutions was determined by potentiometric titration with 0.100 mol dm^{-3} lead nitrate, using an Orion silver/sulfide — DJRE electrode pair (see below).

Preparation of the Wire Ag/Ag_2S Selective Electrodes

A silver wire, 0.7 mm in diameter, containing 2.5—6.0% copper, was inserted into glass tubing and held in place with Elmer's epoxy. Only the end of the wire was exposed. After drying, the end of the wire was hand polished with fine emery paper and immersed for two days in a 0.1 mol dm^{-3} sulfide solution containing SAOB-II. A thin black precipitate film of silver sulfide (as determined by energy dispersive x-ray fluorescence) formed on the surface during this period. The electrodes were then rinsed in deionized water and stored in a saturated solution of silver sulfide prior to use.

Procedure

All potentiometric studies were carried out with an Orion model 601 A digital voltmeter or a Fluke 8000A digital multimeter in a double-walled thermostated cell maintained at 298 ± 0.1 K. The electrodes were connected to the meters through an Orion Research Model 605 electrode switch. An Orion 90—02 double-junction reference electrode (DJRE) with an outer 10% potassium nitrate filler was used as the reference electrode. In comparative measurements, an Orion model 94—16 silver/sulfide electrode was used. A Sargent model 3-30050-15C glass electrode was used for all pH measurements. The Nernstian response measurements for Ag^+ ion were made by serial dilution of the standard 0.1 mol dm^{-3} $AgNO_3$ solution with 0.1 mol dm^{-3} sodium nitrate solution. The sulfide ion solutions were made by serial dilution of the standard 0.1 mol dm^{-3} Na_2S solution, using a 1.0 mol dm^{-3} sodium hydroxide solution (containing 20 mg cm^{-3} ascorbic acid) as the dilution solution. The potentiometric titration studies were carried out in the manner of conventional potentiometric titrations. The titrant was delivered in 0.1 cm^3 steps using a 2.0 cm^3 Gilmont syringe burette. During all measurements the solutions were stirred by means of a Teflon-coated magnetic bar.

RESULTS AND DISCUSSION

Response of the Silver/Silver Sulfide Wire Electrode to Ag^+ and S^{2-}

The equilibrium potentials observed during serial dilution of 0.1 mol dm^{-3} silver nitrate in the measuring cell are plotted against log c_{Ag^+} in curve 1, Figure 1. A linear response with a slope of 57.5 mV per concentration decade (59.0 mV/decade for a theoretical Nernstian response) is obtained in the concentration range from 10^{-1} to less than 10^{-5} mol dm^{-3}, followed by a non-linear region at lower concentrations. The same procedure was used for sulfide ion response plot in alkaline solution containing ascorbic acid. A linear response over a range of $c_{S^{2-}}$ from 0.1 to nearly 10^{-6} mol dm^{-3} with a slope of 28.3 mV per concentration decade (29.5 mV/decade theoretical) was recorded as shown in curve 2, Figure 1. A derivation from linear behaviour is observed in the concentration range 10^{-6} to $< 10^{-7}$ mol dm^{-3}. It should be noted that the data in Figure 1 represent the absolute variation of potential at each concentration for four different electrodes in three separate solutions. The linear response limits of the tested wire electrodes are in good agreement with those observed with Orion silver/sulfide electrode for both silver and sulfide ions[20,21].

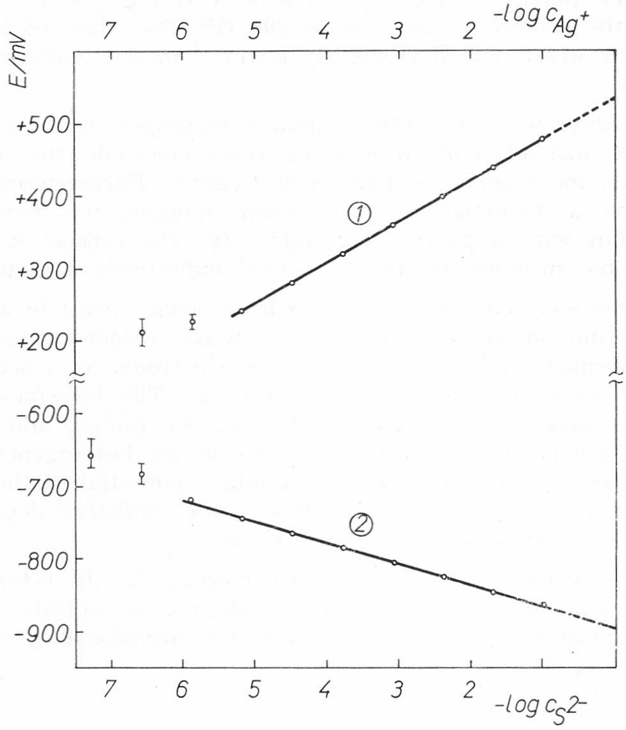

Figure 1. Response of the wire silver/silver sulfide electrode to silver ion and sulfide ion in aqueous solution at constant ionic strength. Curve 1: response to silver ion. Curve 2: response to sulfide ion.

The extrapolated intercepts at log c_{Ag^+} and log $c_{S^{2-}} = 0$ in Figure 1 ($K_1 = 537$ mV and $K_2 = -895$ mV respectively) can be correlated by the expression:

$$K_2 = K_1 + 0.0295\ \log\ {}^{\mathrm{Ag_2S}}_{\mathrm{sp}} \tag{1}$$

The calculated thermodynamic solubility product of silver sulfide is 2×10^{-51}, which is in agreement with the literature values of $6 \times 10^{-50} - 6.2 \times 10^{-52}$ [22,2,18].

Instead of the theoretical Nernstian slope, the experimental slope of curve 2, Figure 1 (28.3 mV) was used in the calculation.

Standard potentials with respect to both silver and sulfide may be found by extrapolating the appropriate potential — log a_{ion} line to log $a_{\mathrm{ion}} = 0$. Activities were calculated from analytical concentrations by use of the extended form of the Debye-Huckel equation[23].

If junction potentials are ignored after correction with 242 mV, as the potential of the reference electrode at 298 K[20], the value of $E^\circ = +787$ mV is obtained for silver, which is sligthly lower than the predicted value (+799 mV vs NHE).

When a silver wire or another metal is employed as the internal contact to Ag_2S pellet, instead of an internal reference electrode, the standard potentials are often more positive than theoretical[24,25]. Furthermore, such M/M_xS electrodes give a Nernstian response when changing the metal ion activity in solution, but with a poorer reproducibility. The contact material usually has little or no influence on the analytical experimental values.

In fact, the electrodes of the second kind, wich consist of a lightly-plated porous Ag_2S film on the surface of silver wires, respond reversibly to ionic activities. Thermodynamically, the Ag/Ag_2S electrode, as a second kind electrode is the same as the first kind electrode. The interfacial potential is determined by means of ion exchange betwen Ag^+ (metal) and Ag^+ (solution). The porous Ag_2S layer only serves to establish the heterogenous equilibrium between solution species Ag^+ and S^{2-}. Standard potential of the Ag/Ag_2S electrode, which differs from the theoretical value, probably depends upon the defect structure and nonstoichiometry of Ag_2S.

By extrapolating to log $a_{S^{2-}} = 0$ and correcting for the reference electrode potential, a value of $E^\circ = -669$ mV is obtained for sulfide. The estimated standard potential is also slightly less than the corresponding $E^\circ = -660$ mV for the following system in base solution[26]:

$$Ag_2S + 2\,e \rightleftharpoons 2\,Ag + S^{2-}$$

It is important to point out here that only the silver wire containing copper in the noted concentration (see experimental section) produced a silver layer after chemical treatment with strong alkaline reducing solution of Na_2S (the SAOB-II contains ascorbic acid and EDTA). When a pure silver wire (99.99% Ag) was used, the black layer on the surface was not observed even after six days of chemical treatment. It appears that the silver sulfide layer is probably produced through an anodic reaction of a localized corrosion process[21]. A SEM micrograph with simultaneous EDAX analysis electrodes showed a uniform deposit of silver sulfide particles (Figure 2) after two days of exposure to sodium sulfide solution. Two other conditions are essential for the formation of a good Ag/Ag_2S selective wire electrode: (i) the presence of the ascorbic acid, which prevents air oxidation of the S^{2-} (no black film is formed even after 6 days on the Ag wire containing the Cu impurity when it is immersed in a de-aerated Na_2S solution in the absence of ascorbic acid, EDTA and NaOH)and (ii) immersion periods shorter than 2 days and longer than 2 days produce electrodes with a less reproducible response and smaller concentration-potential response ranges.

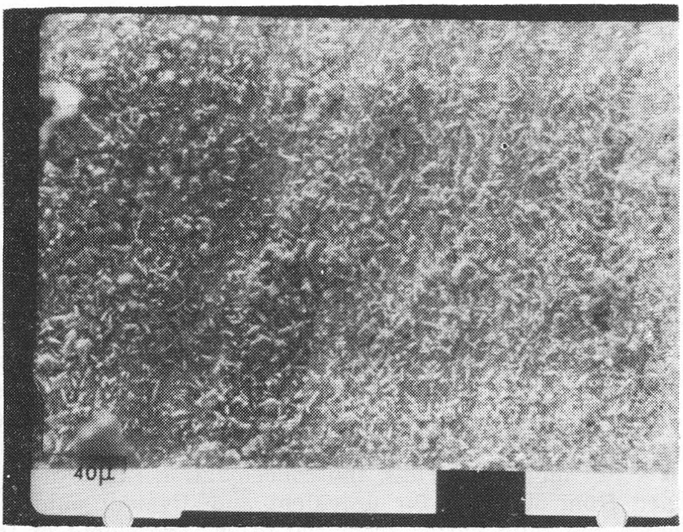

Figure 2. SEM micrograph of the surface of the wire Ag/Ag$_2$S electrode prepared as described in the text.

When the silver wire is dipped into stirred deaerated solutions, saturated with Ag$_2$S powder, constant standard potentials can be observed[27]. The black coating often found on silver articles is also silver sulfide[28], but it is not true that any coating produced by chemical treatment of silver would show good ion-selective behaviour in potentiometric experiments. As it has been pointed out in our work, only a silver wire with uniform deposits of silver sulfide showed a satisfactory ion-selective behaviour.

Response of the Electrode to Other Ions

It is well known that the selectivity of a silver/sulfide membrane is excellent; only mercury cations interfere, as it can be expected on the basis of the solubility products. The selectivity of the Ag/Ag$_2$S electrode was tested by the established selectivity experiments. The selectivity constants, $K_{Ag,M}$, in Table I were calculated using the equation[29]:

TABLE I

Selectivity Constants, $K_{Ag,M}$, *for the Wire Ag/Ag$_2$S Electrode in 0.01 mol dm^{-3} Solutions at pH 3*

Interfering ion (M^{2+})	$K_{\text{Pot.}}^{\text{Ag, M}}$
Co^{2+}	2×10^{-6}
Ca^{2+}	7×10^{-6}
Zn^{2+}	1×10^{-6}
Pb^{2+}	1×10^{-6}
Cu^{2+}	1×10^{-5}

$$\log K_{\mathrm{Ag,\,M}} = \frac{E_{\mathrm{M}} - E_{\mathrm{Ag}}}{57.5} + \log\left[a_{\mathrm{Ag^+}}/(a_{\mathrm{M^{2+}}})^{1/2}\right] \qquad (2)$$

where E_{M} and E_{Ag} denote the electrode potentials, when the sample being 0.01 mol dm^{-3} solutions of the nitrate of the interfering cation and 0.01 mol dm^{-3} $AgNO_3$, respectively. The pH of all the solutions in this experiment was adjusted to pH 3 with nitric acid. The denominator in the above equation is the experimentally determined slope (curve 1, Figure 1). The activities of the ions, a, were calculated using the extended form of the Debye-Hückel equation[23]. The values of $K_{\mathrm{Ag,M}}$ were about 10^{-5} to 10^{-6}, which indicates a high degree of selectivity.

The effects of several anions, namely Cl^-, Br^-, SCN^-, I^-, NO_3^-, $S_2O_3^{2-}$, SO_4^{2-} and $C_2O_4^{2-}$, on the sulfide potential response of the electrode were tested using the mixed solution technique[30] with solutions of 1.0 mol dm^{-3} sodium hydroxide containing ascorbic acid. The test solutions contained a fixed amount of interferent and various sodium sulfide concentrations ranging from 9×10^{-5} to 8×10^{-2} mol dm^{-3}. Thus, the concentration ratios of anions to sulfide ion varied from 500 to 5 for univalent and divalent anions, except for $C_2O_4^{2-}$ for which the ratio varied from 200 to 20. The slopes of the resulting calibration curves, as well as the actual potential values, were in exact agreement, within experimental error, with the response for S^{2-} alone. The above results show that the investigated electrode can be used for selective analytical measurements in a wide variety of practical systems.

In another experiment, at constant total sulfide concentration and constant ionic strength, the potential dependence, as a function of pH, was examined. A plot of this data should exibit two slopes[2,31–33]. Figure 3 shows that the pH response of the commercial silver/sulfide electrode and the wire Ag/Ag_2S

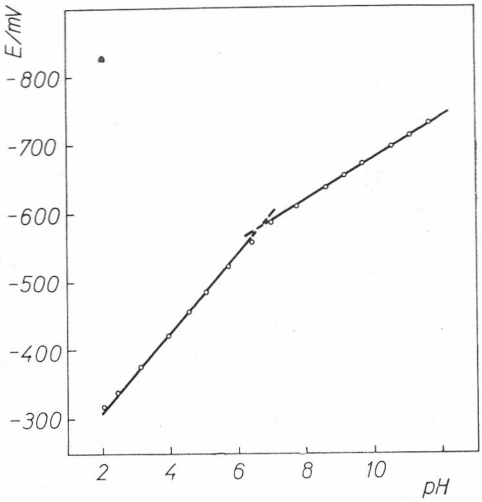

Figure 3. The potential — pH response for Ag/Ag_2S electrodes at constant ionic strength. The concentration of Na_2S was 4×10^{-4} mol dm^{-3}. The Orion silver/sulfide electrode response is given by solid line. The wire Ag/Ag_2S electrode response is given by circles.

electrode are essentially the same .The experimentally calculated slopes for the wire silver/silver sulfide electrode were 56.7 ± 0.2 and 30.4 ± 0.3 for acidic and alkaline regions, respectively. The slope values were calculated and averaged for three total sulfide concentrations in the range of 10^{-4} to 10^{-3} mol dm^{-3} and four different wire electrodes. The pH was changed from 2 to 12 by mixing 4×10^{-2} mol dm^{-3} of acetic, boric and phosphoric acids with the necessary volume of 2 mol dm^{-3} sodium hydroxide. The eletcrolysis solution was initially 0.1 mol dm^{-3} in $NaNO_3$.

Lifetime and Storage of the Electrode

As discussed, the large number of ions in the test solutions do not disturb the potential response of the electrode to sulfide or silver ion, and do not cause any degradation of the electrode itself. However, when the electrode is used repeatedly in copper(II) solutions, the response changes and a new sulfide layer deposits on the surface and partial dissolution of the silver sulfide layer occurs. This effect shortens the life of the electrode. Similarly, after even a short exposure to Hg^{2+} ion, the Ag_2S layer was totally destroyed and the electrode selectivity was lost (this effect is discussed below in the potentiometric titration section). Generally, after preparing the electrodes and use, the electrodes were stored in distilled water saturated with silver sulfide. However, it was found that a prolonged dry storage of electrodes in the air (up to one week) had no measurable effect on their responsees.

Potentiometric Titrations

The wire electrode was also tested as an end-point indicator electrode in potentiometric titrations involving Ag^+ or S^{2-} ions. For comparison, the titrations were followed simultaneously with more wire Ag/Ag$_2$S and commercial silver/sulfide electrodes. The shape of the potentiometric titrations of Ag^+ ions and the actual potential values near and after the end points were in excellent agreement (see Figure 4.). Also, the comparison of the potentiometric

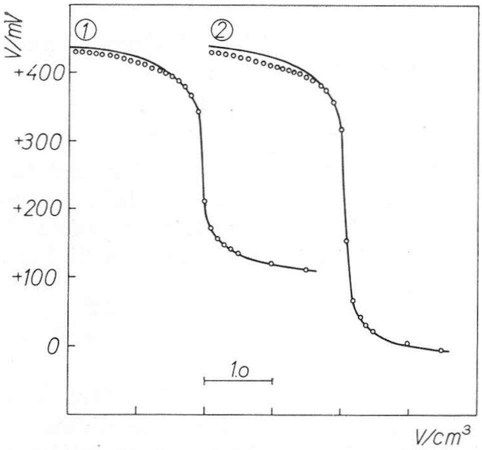

Figure 4. Ag(I) titration with 0.1 mol dm^{-3} Cl^- (1) and 0.1 mol dm^{-3} SCN^- (2). The Orion silver/sulfide electrode response is given by solid lines. The wire Ag/Ag$_2$S electrode response is given by circles.

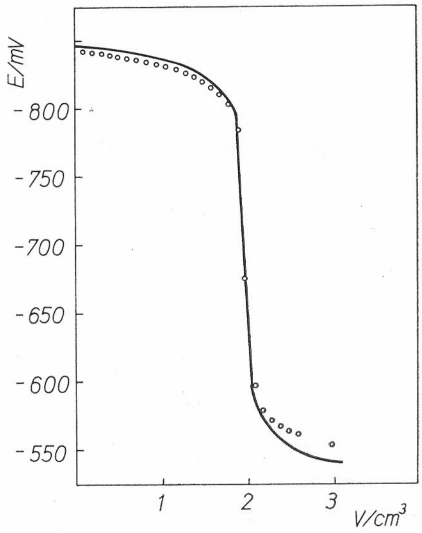

Figure 5. Sulfide titration in alkaline solution with 0.1 mol dm^{-3} Pb^{2+}. The Orion silver/sulfide electrode is given by solid line. The wire Ag/Ag_2S electrode is given by circles.

titration of sulfide with Pb^{2+} in alkaline solution (Figure 5) indicates that the titration curve and the end point observed coincide acceptably. However, the total potential break is slightly less than the break of the commercial electrode.

When the wire silver/silver sulfide electrode is immersed in the solution containing divalent metal ions (Cu^{2+}, Cd^{2+}, . . .) , the metal sulfide may be precipitated on the silver sulfide surface:

$$Ag_2S(s) + M^{2+} \rightleftharpoons MS(s) + 2\,Ag^+ \tag{3}$$

The relation between the activities of silver(I) and metal(II) ions may be expressed by the next simple relation:

$$a_{Ag^+} = (a_{M^{2+}} \cdot K_{sp}^{Ag_2S}/K_{sp}^{MS})^{1/2} \tag{4}$$

If the concentration of the metal ion in solution and the solubility constant are sufficient for reaction 3 to proceed to the right, the activity of silver ions on the surface is determined by the activity of metal ions in test solution and consequently the potential of the electrode will be:

$$E = E^0_{Ag^+,\,Ag} + \frac{RT}{2F}\ln\frac{K_{sp}^{Ag_2S}}{K_{sp}^{MS}} + \frac{RT}{2F}\ln a_{M^{2+}} \tag{5}$$

In order to confirm this possibility, the wire silver/silver sulfide electrode was used as end-point indicator for the potentiometric titration Cu^{2+} ion with EDTA in buffered solution (sodium acetate buffer pH 4). For the mentioned system, a typical potentiometric titration with a fresh wire Ag/Ag_2S electrode exhibits the classical shape and a sharp potential break, as shown

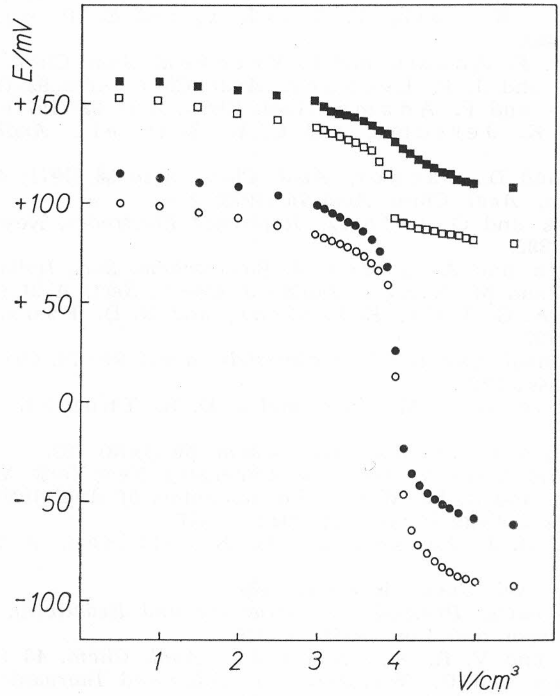

Figure 6. Cu(II) titrations with 0.05 mol dm^{-3} EDTA at pH 4 followed by the wire Ag/Ag$_2$S electrode. The titration with a fresh wire electrode, —○—. After prolonged storage in Cu^{2+} solution, —●—. The same titration after soaking the electrode in 0.01 mol dm^{-3} Hg^{+2}; one minute —□— and five minutes —■—.

in Figure 6. The total potential break was less but the equivalence point volume was essentially the same when the electrode was used after one day storage in 0.1 mol dm^{-3} Cu^{2+} solution before titration. However, the mercury(II) ion, even in short contact, attacks the wire silver sulfide layer of the electrode and is not applicable as an indicator electrode (Figure 6). The commercial silver/sulfide electrode also shows degradation in the presence of Cu^{2+} and Hg^{2+} but at a much slower rate. Thus, the wire Ag/Ag$_2$S electrode is not applicable to the routine titration of metal ions, for which reaction 3 proceeds far to the right.

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SAŽETAK

Selektivna Ag/Ag_2S elektroda

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Opisani su uvjeti priprave i izvedba selektivne Ag/Ag_2S-elektrode malih dimenzija. Analitičko ponašanje elektrode, pripravljene kemijskom obradbom srebrne žice, opisano je s pomoću krivuljâ potencijal-koncentracija, standardnog potencijala, vremena života i selektivnosti. Pripravljen je i ispitan niz elektroda, a njihov odziv i selektivnost prema S^{2-} i Ag^+ uspoređeni su s komercijalnom Orion Ag/Ag_2S--elektrodom. Izvedeno je nekoliko titracija radi ocjene rada elektrode. Ispitivana elektroda može se upotrijebiti kao dobra zamjena komercijalnoj Ag/Ag_2S-elektrodi, u vrlo raznolikima praktičnim analitičkim sustavima.