SPER
Publications and Solutions Pvt. Ltd.

Original Article

Fabrication of a sulfide ion-selective electrode and study of its electrochemical characteristics

Ronak Ramezani[1]*, **Farzad Bamdad**[1]

[1]Department of Analytical Chemistry, Arak University, Arak Iran.

Correspondence: Ronak Ramezani, Department of Analytical Chemistry, Arak University, Arak Iran. Ronakrmz9august@gmail.com

ABSTRACT

Sulfur anions, including sulfide ions, are greatly important chemically, industrially, and environmentally. The reactivity nature of sulfide ions is the main problem in the measurement of this anion. Thus, the use of rapid, selective, and cheap methods to determine this species is an important aspect of controlling industrial processes and protecting the environment. In the present study, a simple method for the fabrication of a sulfide ion-selective electrode has been proposed. Parameters that are effective on measurements such as time, effect of interfering ion, and pH were investigated. The grading curve in this method has a linear range from 10^{-5} to 10^{-1} mol/L, and the percentage of relative standard deviation is 1.3%, with a detection limit of 10^{-7} x 5.1 mol/L. Simple and available laboratory equipment, appropriate sensitivity, and low cost are important advantages of this method.

Keywords: Sulfide, Ion-selective electrode, Potentiometry, Electrochemistry

Introduction

After the discovery of the pH-sensitive glass electrode, the fabrication of the selective ions was evaluated [1]. It seems that development in the area of exchange was initiated in the 1930s by Nicolsky [2]. Yet, many materials have been investigated as selective ion membranes. Scientific research in 1950 was a motivation for development of the ion-selective electrodes. Some ion-selective electrodes have been developed since 1960 [3]. Numerous methods can measure ions in aqueous solutions such as UV-Vis spectroscopy, Flame atomic absorption spectrometry (FAAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), Coupled Plasma Mass Spectrometry, Fluorescence and Phosphorescence, High-Performance Liquid Chromatography (HPLC), Electrophoresis, and Voltammetry. These methods are highly selective. However, the high costs, device complexity, and time consumed for analysis make us turn to Ion-Selective Electrodes (ISEs), which are the most important group of potentiometry sensors. Recently, the use of these electrodes has grabbed a lot of attention due to their simplicity, cheapness, sensitivity, selectivity, and precision compared to other methods and measurement devices used in analytical chemistry [4]. Glass electrode was the first ISE studied. In 1909, Heber designed bulb-shaped glass electrodes. In 1930, Bekman designed pH glass electrodes with rudimentary tools such as voltmeters. Afterward, with Kolthoff's studies in 1937, it was more developed. However, until 1991 when Pungor's studies and articles were not yet published, these electrodes had not grabbed a lot of attention. In 1996, Moor & Persman [5] showed that antibiotics can transfer the ions in the mitochondria, and after this exploration, Simon and Stephens [6, 7] showed in 1996 that this phenomenon can create selective complexes between these compounds and specific cations. Accordingly, they introduced the first neutral ISE-based carrier. Pedersen and Lahman [8, 9] synthesized large ring polymers and compounds of large heterocycles and showed that these compounds can be used as complexing agents for alkali and alkaline earth metal ions.

Shotki and Ross played an important role in the development of the liquid-membrane ISEs. They proposed a polymer solvent membrane. Ross introduced the first calcium cation-sensitive liquid membrane. Accordingly, the design of different species of ion-selective electrodes with various applications has continued until today it has become one of the most important research fields [10, 11]. Glass electrodes respond to single-charged ions. The reason behind choosing these electrodes for single-charged cations is the change in the thin ion-sensitive glass membrane compound. The basic part of these electrodes is covered with a thin layer of glass with a special composition, which is placed on its noise a basic component of the electrode. This thin layer, which contains fixed groups of anions (Silicate) and exchangeable mobile cations, plays the role of an exchange membrane. Due to the same behavior, when such membrane is placed between two M^+-cation-contained solutions to which the membrane is sensitive, a potential difference is created between each of the two sides of the membrane and the solution, which can be shown by placing a reference electrode in each of the two solutions placed on both sides of the membrane and measuring the potential difference between the two electrodes [12].

In using the pH glass electrode, it has been mentioned that alkaline solutions cause interference in response to pH. Therefore, changes calculated in the chemical compound of the glass lead to the fabrication of responsive electrodes to single-charged cations other than hydrogen, such as sodium, ammonium, and potassium. It usually requires an increase in B_2O_3, Al_2O_3, and 71% Si_2O [13]. The general mechanism of electrode response is complex, however, it includes a combination of ion exchange phases on the surface and ion distribution. To further decrease the hydrogen's ion interference, we'd better use solutions containing pH values above 5. Modified electrical and mechanical characteristics can be obtained through the use of very complex glasses that contain various additives. For example, Kimura *et al*. for the first time, fabricated a Sol-Gel-based modified glass-membrane electrode that contained neutral carriers to measure the anions [14].

The interest in the investigation of the electrochemical behavior of sulfides is increased due to heterogenous rotational reactions in nature. On the other hand, metal sulfides are suitable for ion-selective electrodes and sulfur batteries. One of the most desirable metal sulfides is silver sulfide which is developed as an ISE [15]. The first thing done on the silver sulfide electrode is the thermodynamics of type II electrodes, the electrical double layer, and silver sulfide composites. Jaenicke *et al*. [16] conducted an electrochemical study on silver sulfide because solid ionic conductors were considered options for energy generation and storage. Iodometric methods and methylene blue colorimetry are among the most important methods for sulfide measurement. The iodometric method is based on the iodine-sulfide reaction and sulfide oxidation, suitable for analysis of the sample with high concentrations of sulfide. Colorimetry is a very sensitive method used for the analysis of wastewater. However, due to the matrix interference in this method, it is less used [17, 18].

Through electrochemical detection, ionic chromatography was successfully investigated by Ranklin and Johnson. Electrochemical-based IC and UV detection are common methods to measure ion sulfide, especially in the alcoholic drinks and paper industry [19]. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) is used to measure sulfide compounds [20]. This method was tested by Nakahara *et al*. in a way that the sample is introduced in the form of gas to be used for the measurement of sulfide and sulfite in aqueous samples [21]. Another method for measurement of ion sulfide is Flow Injection Analysis (FIA). The validity of this method was first tested by Francis and Taylor and then was reinvestigated by Ali Ensafi [22].

To date, the potentiometry of small amounts of sulfur in solid samples has been performed by reducing the solid sample and absorbing the formed $H_2S(g)$ in a suitable solution (stable and resistant to oxidation). Therefore, the total amount of sulfur is measured directly through potentiometry titration by a sulfide ion-selective electrode. Yet, all methods reported have been conducted through standardization of the solid samples of sulfur, so that the error made due to sulfur wastage during the long titration process can be avoided. This wastage is highly important, especially in concentrations below 3×10^{-3}.

Studies on ISEs include a wide range of research and are developing rapidly. Krueger directly measured sulfurs using gas-sensitive electrodes which were ion-selective compared to SO_2 and other species of acidic sulfurs, by collecting combustion products in an absorbent solution [23]. Also, the use of chloramine-T (CAT) membrane ISE can allow for indirect measurement of reducing agents such as sulfide and thiosulfate. Baumann, using pre-concentration of sulfur and detecting it by sulfide ISE, managed to measure low amounts of sulfide (at ppb level). In this method, sulfide is separated as zinc sulfide and in the next step, it is measured by potentiometry by dissolving the sediment in the alkaline solution of SAOB buffer.

Determination of elemental sulfur, sulfide, and its mixture in the electrolyte solution is done using voltammetry. An Amperometric sensor for sulfide hydrogen based on sulfide hydrogen oxidation to sulfur by redox mediator $[\mathrm{Fe(CN)_6}]^{3-}/[\mathrm{Fe(CN)_6}]^{4-}$is the basis of this method.

Also, colometric calibrations allow for the measurement of hydrogen sulfide in aquatic samples. This method is a linear determination of H_2S between 1 to 750 μmol/L with an injection volume of 28 μ. Factors such as flow rate, gas injection volume, and pH affect the test process [24].

Modern polarography methods are very suitable for sulfur species. Normal and differential pulse polarographic methods are used in combination with different spectroscopic and chromatographic techniques to present information about the concentration, nature, origin, distribution, and behavior of sulfur species in various natural lake waters that have undergone oxygen reduction due to biological activities, in food (usually the fruits and vegetables), and in oil products. The basis for the determination of low amounts of sulfide in elemental sulfur in reversible electrochemical processes is the exchange of two electrons [25].

In 1955, James measured sulfide using conductometry. This method is based on sedation by silver nitrate 0.55 solution. Thiosulfate interfered in this test [26]. In 1956, Sato used the volumetric titration to measure sulfide. In this method, Eriochrome Black T was used as the indicator for titration by zinc sulfate. In this method, iron, magnesium, and manganese are considered as interfering effects [27]. a new titration method was proposed by Norris *et al* for the determination of sulfide amount using silver nitrate. In this method, a rotating silver-silver sulfide detector electrode is used to identify the endpoint [28]. In 2002, a methylene blue potentiometric sensor was proposed by Hassan *et al*. to measure sulfide ions [29]. In 2021, Bautista et al proposed a 3D-printed and fully portable fluorescent-based platform for sulfide determination in water [30]. In 2021, Yuan *et al*. proposed a method for the detection of nanomolar sulfides soluble in water by coupling the classic methylene blue method with Raman scattering detection [31].

Since sulfide is chemically, industrially, and biologically important, and plays a significant role in environment protection. High amounts of sulfide can cause irreparable consequences for nature and human beings. Detection and measurement of this anion has been much debated in scientific communities. The present study aimed to propose a simple, cost-effective, valid, and precise method for the detection and measurement of the sulfide in a short time with the use of available and portable laboratory equipment and application of an ISE with acceptable reproducibility by potentiometric method.

Materials and Methods

Reagents included materials with analytical purity and without the need for further purification. To prepare and increase the dilution of these solutions, double-distilled water with a conductivity of 1.4 microsiemens/cm has been used in all stages.

Preparation of sulfide antioxidant buffer (ASOB)

The SAOB solution was used due to the instability of sulfide and its oxidation with oxygen. It is an alkaline solution and provides a high pH antioxidant media to retain sulfide ions in calibration standards and test samples during analysis with sulfide ISEs. In the present study, this ligand salt was prepared using the Na2EDAT 0.1 M, NaOH with a concentration of 0.1 M, and ascorbic acid with a concentration of 0.01 M. This buffer was prepared fresh, daily.

Preparation of salt bridge

To prepare the salt bridge, first, 1 gram of agar was mixed with 2.5 grams of potassium nitrate in 25 mm of double distilled water. The temperature was controlled in a 60-70 degrees Celsius range using a mercury thermometer.

Preparation of ISE

A silver wire with a purity of 99% and a diameter of 1 mm was used to make the electrode. As shown in **Figure 1**, the silver wire was soldered to a piece of copper wire by placing it at the end of a glass tube with an inner diameter of 1 mm.

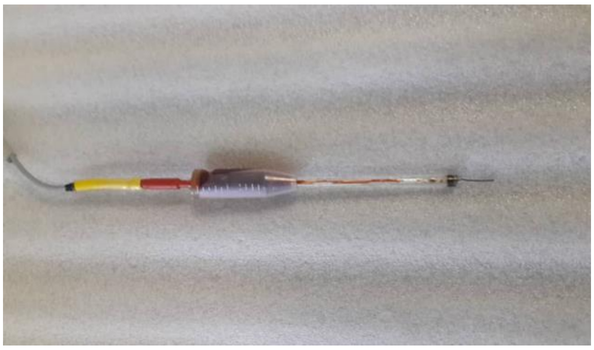


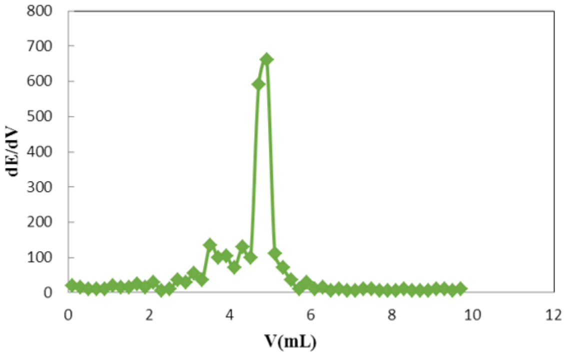
Figure 1. The ISE prepared in the present study

Results and Discussion

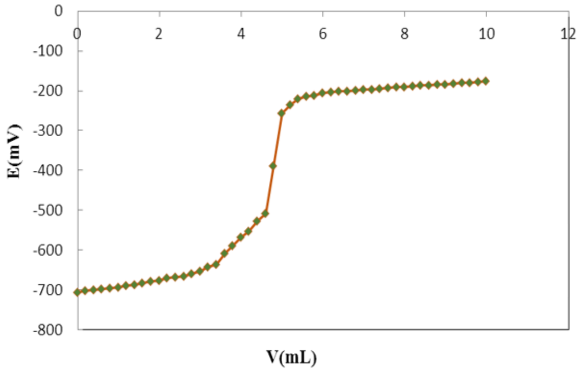
To measure the sulfide ion (5ml), cadmium salt was used as a titrant (with a concentration of 0.01 molar). According to Eq. 1, the concentration of S^{2-} was obtained to be 0.0098 m/Lit. **Figure 2** shows the yellow-orange sediment resulting from this titration, **Figure 3a** shows the diagram of potentiometric titration, and **Figure 3b** shows the diagram of the first derivative of potentiometric titration to obtain the endpoint of the titration more precisely.

$$\mathrm{Cd(NO_3) + Na_2S \leftrightarrow CdS + 2NaNO_3} \qquad (1)$$

Figure 2. Yellow-orange precipitate obtained from titration of sulfide with cadmium



a)



b)

Figure 3. a) Potentiometric titration of 5 ml of sodium sulfide with an approximate concentration (0.01 M) by 0.01 M cadmium nitrate. b) The first derivative of the potentiometric titration of 5 ml of sodium sulfide with an approximate concentration (0.01 M) by 0.01 M cadmium nitrate

By placing the ISE in $HgCl_2$ and Na_2S in a period of 15-60 mins, no significant difference was observed in the ISE response. Therefore, the 15-min period was chosen as the optimal period **(Table 1)**.

Table 1. The placement time of the sulfide ISE in HgCl2 and Na2S solutions

The duration of placement of the sulfide ISE in the solutions	Sulfide ion selective electrode response E(mV)-
15	707
30	707
45	696
60	701

Regarding the diagram of species distribution shown in **Figure 4**, in more alkaline pH values (above 10), the amount of S^{2-} is increased and vice versa. In pH values above 7, HS^- is decreased rapidly. Then, with the increase in pH, its value is increased, and, in the values close to 11 (pH=11), its value is decreased. In this diagram, to obtain the concentration of hydronium ion, pH metering was done and based on the read pH, and after the addition of specified volumes of cadmium nitrate, the curve of pH titration was plotted as shown in **Figure 4**.

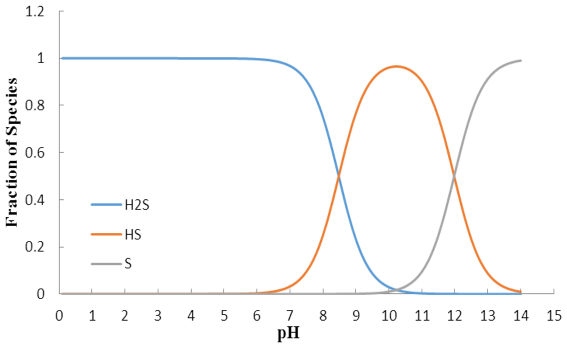


Figure 4. Diagram of species distribution

In the present study, potentiometry was done alongside pH metering. Titration of Na_2S by 0.1 molar cadmium acetate in the presence of salt bridge, Calomel electrode as a reference electrode, and sulfide ISE (as a detector electrode). Using Eqs. 2 to 5, values of α_0, α_1 and α_2 as well as the value of $[H^+]$ were calculated by pH metering, and the distribution diagram of three species H_2S, HS^-, and S^{2-} were plotted.

$$[H^+] = 10^{-pH} \tag{2}$$

$$\alpha_0 = \frac{[H^+]^2}{[H^+]^2 + [H^+]k_1k_2} \tag{3}$$

$$\alpha_1 = \frac{[H^+]^2}{[H^+]^2 + [H^+]k_1 + k_1k_2} \tag{4}$$

$$\alpha_2 = \frac{k_1k_2}{[H^+]^2 + [H^+]k_1 + k_1k_2} \tag{5}$$

To plot the calibration curve, the stock solution Na_2S with concentrations of 10^{-5} to 10^{-1} molar was prepared. A specified volume of solution was poured into the beaker, and in the presence of the sulfide ISE and the calomel electrode, the potential was read on the Titroprocessor. To plot the curve, the experiment was repeated five times and the obtained calibration curve was plotted in terms of (pS^{-2}-log[S^{-2}])

To investigate the reproducibility of the sulfide ISE, first, it was placed in 0.1 molar $HgCl_2$ for 15 minutes to be then washed with double-distilled water. After that, it was placed in a 0.1 molar Na_2S solution. The measurement of sulfide ion in the stock solution was repeated 5 times, using the prepared electrode. The results indicate that the fabricated sulfide ISE has an acceptable reproducibility. The relative standard deviation percentage was obtained to be 8.84%. Therefore, by the use of the fabricated electrode, the concentration of sulfide ions can be measured with good precision.

To investigate the effects of interferences, Anionic and cationic resins of different salts were tested in a way that the stock solution Na_2S with a concentration of 0.001 molar was prepared. Interfering species were also prepared with a concentration of 0.01 molar. Some of the solution was poured into the beaker and in the presence of a salt bridge, calomel electrodes as reference electrodes, and sulfide ISEs as detector electrodes, the device potential was read. Then, the Nicolsky-Eisenman Equation (Eq. 6) was used to show the selectivity of Species A in the presence of interfering species. Calculations done are shown in **Table 2**. In the Nicolsky-Eisenman Equation, the selectivity coefficient of Species A (sulfide ion) in the presence of interfering species was calculated. Results are shown in **Table 2**.

$$K^{pot}_{A.B} = \alpha_A(e^{\Delta E.Z_A F/RT} - 1)/\alpha_B{}^{Z_A/Z_B} \tag{6}$$

$K^{pot}_{A.B}$: Selectivity coefficient of Species A (Sulfide ion in the present study)

Z_A: Charge of Species A (sulfide ion)

Z_B: Charge of Species B

R: Gas constant=8.314 J/mol.K

F: Faraday constant=96485 C/mol

α_A : Molar concentration of Species A (Sulfide ion)
α_B: Molar concentration of interfering Species B
T: Temperature per Kelvin (K)

Table 2. Selectivity constants calculated for sulfide ISE in the presence of interfering anionic and cationic agents

$K^{Pot}_{A,B}$	Cationic resin	$K^{Pot}_{A,B}$	Anionic resin
4.15×10^{-6}	Cr^{3+}	0.97	$S_2O_3^{2-}$
1.85×10^{-6}	Ni^{2+}	0.80	I^-
-1.00×10^{-5}	Cu^{2+}	-0.08	CrO_4^{2-}
-1.00×10^{-5}	Co^{2+}	0.13	CO_3^{2-}
-1.00×10^{-5}	Cd^{2+}	8.87×10^{-3}	CH_4N_2S
5.29×10^{-8}	Na^+	8.87×10^{-3}	$C_2O_4^{2-}$
5.29×10^{-8}	K^+	0.89	SCN^-
0.40×10^{-5}	Ca^{2+}	0.05	SO_3^{2-}
0.93×10^{-2}	Fe^{2+}	-5.34	HCO_3^-
-0.87×10^{-5}	Mg^{2+}	-5.3×10^{-3}	OH^-
-9.99×10^{-8}	Li^+	-3.99	NO_3^-
-0.97×10^{-7}	Ba^{2+}	-	Cl^-
4.1496	Ag^+	-	SO_4^{2-}
		-	F^-
		-	Br^-

As shown in **Table 2**, among the anions, bromide, chloride, fluoride, and sulfate ions do not interfere with sulfide measurement using the ISE, while thiosulfate ions cause the most interference. In the present study, thiourea was also investigated because it is an organic compound of sulfur. However, it did not cause a significant interference. Among the cationic resins, sodium and potassium ions caused little interference, while the most interference was caused by silver ions. The negative sign in the selectivity constant indicates that the ISE is more selective than the interfering ion. According to **Table 2**, the sulfide ISE showed more selective behavior in this research than chromate, bicarbonate, hydroxide, nitrate, copper, cobalt, cadmium, magnesium, lithium, and barium ions.

In this phase, the time required for the device to show a constant value was investigated, and this period was used as the best duration to end the process in the present study. The process includes pouring an amount of stock solution Na_2S with a specified concentration into a beaker and adding sulfide ISE and calomel electrode to the mixture to investigate sulfide ISE's response in durations 0 to 24 minutesThe 10-minute duration was chosen as the optimal time for potential fixation.

Table 3. Sulfide ion concentration obtained in real samples

by classical iodometric method		
Sulfide ion concentration in real samples	Well water in the Shazand region 0.702 mg/Lit	Mashhad Leather Factory wastewater 25 mg/Lit
the fabricated ISE in the present study		
	Well water in the Shazand region	Mashhad Leather Factory wastewater
Sulfide ion concentration in real samples	0.732 mg/Lit	25.5 mg/Lit

Conclusion

In the present study, the fabrication of a sulfide ISE by the use of available and inexpensive laboratory equipment was investigated. The sulfide ion concentration in real samples was measured using the fabricated electrode and potentiometry method. Considering the results obtained, this electrode showed a relatively proper response speed as well as acceptable precision and validity. To investigate the application of the electrode, the sulfide amount was measured in several real samples of well water in the Shazand region and Mashhad Leather Factory wastewater.

Acknowledgments: None

Conflict of interest: None

Financial support: None

Ethics statement: None

References

1. Hilwa WR. Clinical Instrumentation Refresher Series: Ion Selective Electrodes. Med TechNet Online Services. 1998:1-6.
2. Nicolsky BP. Theory of glass electrodes. Zh Fis Khim. 1937;10(495):487.
3. Gulaboski R, Mirceski V, Komorsky-Lovric S. Electrochemistry in the twenty-first century—future trends and perspectives. J Solid State Electrochem. 2020;24:5-6.
4. Bard A, Faulkner LR. Electrochemicalmethodes: Fundamental & applications. Wiley; 2001. pp.1-44.
5. Moore C, Wallis C, Melnick JL, Kuns MD. Photodynamic treatment of herpes keratitis. Infect Immun. 1972;5(2):169-71. doi: 10.1128/iai.5.2.169-171.1972
6. Simon W, Morf WE, Meier PC. Specificity for alkali and alkaline earth cations of synthetic and natural organic complexing agents in membranes. InAlkali Metal Complexes with Organic Ligands 2005 Sep 26 (pp. 113-160). Berlin, Heidelberg: Springer Berlin Heidelberg.
7. Stephens A. Cryptates and pendant arm ligand complexes (Doctoral dissertation, [University of Adelaide]). [Australia], 1994.
8. Pedersen CJ. The discovery of crown ethers. Science. 1988;241(4865):536-40.

9. Lehman-Andino I. Dipicolinamide Ligands and Analogs for Lanthanides (Ln), Actinides (An) and Mercury (Hg) for Application to Nuclear Fuel Cycle Separations and Waste Management. 2020.
10. Shatkay. Ion specific membranes as electrodes in determination of activity of calcium. Analytical Chemistry. 1967;39(10):1056-65.
11. Ross JW. Calcium-selective electrode with liquid ion exchanger. Science. 1967;156(3780):1378-9.
12. Bockris J O'M, Conway BE. Modern electrochemistry. Springer Link. 1998;1:2-32.
13. Ganjbakhsh Sanati M, Khorsandi Chenarboo M. Carbon paste electrode design using nanoparticles based on 1,2-bis(2-hydroxybenzamido)-5,4-dimethylbenzene as an ion carrier. Miyad Publishing House, Tehran, first edition; 2011.
14. Kimura K, Yajima S, Takase H, Yokoyama M, Sakurai Y. SoI--gel modification of pH electrode glass membranes for sensing anions and metal ions. Anal Chem. 2001 Apr 1;73(7):1605-9. doi:10.1021/ac001434f. PMID: 11321316.
15. Haber F, Klemensiewicz Z. First glass electrode and its creators. Phys Chem. 1909;67:385.
16. Lim GS, Zidar J, Cheong DW, Jaenicke S, Klähn M. Impact of ionic liquids in aqueous solution on bacterial plasma membranes studied with molecular dynamics simulations. J Phys Chem B. 2014 Sep 4;118(35):10444-59. doi:10.1021/jp5060952
17. Mourizina YG, Schubert J, Zander W. Development of multisesensors systems based onchalcogenide thin film chemical sensors for the simultaneous multicomponent. Electrochem Acta. 2001;47:251-8.
18. Moore C, Pressman BC. Mechanism of action of valinomycin on mitochondria. Biochem Biophys Res Commun. 1964;15:562-7.
19. Rocklin RD, Johnson EL. Determination of cyanide, sulfide, iodide, and bromide by ion chromatography with electrochemical detection. Analytical Chemistry. 1983 Jan 1;55(1):4-7.
20. Štefanac Z, Simon W. Ion specific electrochemical behavior of macrotetrolides in membranes. Microchem J. 1967;12(1):125-32.
21. Nakahara T, Mori T, Morimoto S, Ishikawa H. Continuous-flow determination of aqueous sulfur by atmospheric-pressure helium microwave-induced plasma atomic emission spectrometry with gas-phase sample introduction. Spectrochimica Acta Part B: Atomic Spectroscopy. 1995 Jun 1;50(4-7):393-403.
22. Kazemzadeh A, Ensafi AA. Sequential flow injection spectrophotometric determination of nitrite and nitrate in various samples. Analytica chimica acta. 2001 Sep 5;442(2):319-26.
23. Cremer M, Biol Z. The seventies-Golden age for ion selective electrodes. Chem Educ. 1997;74:167.
24. Zorrilla LA, Calvo JG. Monitoring system for ISFET and glass electrode behavior comparison. In2017 IEEE XXIV International Conference on Electronics, Electrical Engineering and Computing (INTERCON) 2017 Aug 15 (pp. 1-4). IEEE.
25. Kukizaki M, Nakashima T. Acid leaching process in the preparation of porous glass membranes from phase-separated glass in the Na2O-CaO-MgO-Al2O3-B2O3-SiO2 system. Membrane. 2004;29(5):301-8.
26. Mikula JJ, Codell M. Polarographic Determination of Copper, Nickel, Cobalt, Manganese, and Chromium in Titanium Alloys. Analytical Chemistry. 1955 May 1;27(5):729-32.
27. Sato M. Oxidation of sulfide ore bodies; 1, Geochemical environments in terms of Eh and pH. Economic Geology. 1960 Aug 1;55(5):928-61.
28. Norris PR, Kelly DP. Toxic metals in leaching systems. Metallurgical Applications of Bacterial Leaching and Related Microbiological Phenomena, New Mexico. 1978;1978.
29. Hassan SS, Marzouk SA, Sayour HE. Methylene blue potentiometric sensor for selective determination of sulfide ions. Analytica Chimica Acta. 2002 Aug 21;466(1):47-55.
30. Leal VG, Batista AD, Petruci JFDS. 3D-printed and fully portable fluorescent-based platform for sulfide determination in waters combining vapor generation extraction and digital images treatment. Talanta. 2021 Jan 15;222:121558.
31. Li P, Yuan D, Lin K. Determination of nanomolar dissolved sulfides in water by coupling the classical methylene blue method with surface-enhanced Raman scattering detection. Spectrochim Acta A Mol Biomol Spectrosc. 2021 Mar 5;248:119162.