High Sensitivity Sulphite Membrane Selective Electrode and its Application

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Summary: In this study, the new sulphite sensitive ion-selective electrode (ISE) was prepared. The ISE was prepared from a combination of 5% perfluorooctanesulfonic acid (PFOS), 40% PVC and 55% dibutylphthalate (DBF).The sensitivity of the ISE to $1.0x10^{-7}$-$1.0x10^{-1}$ M sulphite concentration was 58 ± 4 mV. Electrode sensitivity was characterized. The response time of this electrode is short and 30 s. The lifetime of ISE was approximately 210 days when used five times a day. It was determined that it can work at any pH value. It is not sensitive to anions and cations that may be present in the determination medium. The detection limit of the electrode against the sulfide concentration was measured as $1.2x10^{-8}$ M. The amount of sulfites in dried apricots in Turkey, was measured with electrodes. Sulfite amount in dried apricot was determined as 2.328 ± 0.2417 mg / kg according to the average of 5 experiments and 95% confidence interval. The same sample was measured with DPP as 2.521 ± 0.2785.The validation of the obtained results in each case was proved by statistical "t" and "F" tests.

Keywords: Sulphite selective electrode; Membrane; Dried apricots.

Introduction

Sulphite is used as a food additive. It is mostly used to protect the flavor and color of foods, to prevent the growth of bacteria, to reduce spoilage, to prevent discoloration or browning of fresh foods, as well as to help preserve medicines and extend their shelf life [1].They release the active ingredient, sulfur dioxide, and this component has been shown to cause narrowing of the bronchi in the lungs [2]. Therefore, sulfide determination becomes important.

Many methods are used for sulfide determination in the literature. Sulphite was determined in wine by flow injection method [3, 4].The amount of sulfide in natural waters was determined by subtracting the sulfur concentration measured by ion chromatography from the sulphate concentration measured by potentiometric method [5]. Lowinsohn and Bertotti determined approximately 0.4-1.2 mM sulphide content in white wine by the coulometric method [6].

Electrochemical methods have many advantages over other methods such as high sensitivity, very low detection limits and low interference effect. With these electrochemical methods, analysis of trace elements, vitamins and proteins are performed [7-9]. Sulfite is also determined by electrochemical methods. In the determination of sulfur with an electrochemical sensor created by modifying the glassy carbon electrode, it was determined using cyclic voltammetry [10], square wave polarography [11] and differential pulse polarography [12-14].

Ion-selective electrodes have advantages over other methods due to their good selectivity, not being sensitive to other ions, being easy to prepare and being a cheap method [15]. Ion selective electrodes were also used for sulfide determination. In these assays, ion-selective electrodes sensitive to other ions were used instead of sulfur electrodes. Iodide-SE [16], lead-SE [17], silver sulphidetrode [18], cadmium-SE [19] was used in the determination of sulphite.

In this study, the new a sulfide sensitive membrane selective electrode was developed for the first time. An electrode with high selectivity and sensitivity, cheap to prepare, and not sensitive to other anions and cations in the analysis medium was made. This electrode was used to measure the amount of sulfide in the real sample.

Experimental

Reagents

The solutions used in the study were prepared with triple water and sodium nitrate was used to keep the ionic strength of the environment constant. Brands of PFOS (Perfluorooctanoic acid), PVC (polyvinylchloride), DBF (dibutyl phthalate) and other reagents are Sigma-Aldrich.

Apparatus

For potential measurements, Orion Star A214 pH/ISE Benchtop meter, reference electrode and IKA Plate magnetic stirrer mixer were used.

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Preparing Membrane Electrode

A mixture of 5% PFOS [16], 40% PVC and 55% DBF plasticizer, with a total mass of 0.3 g, was dissolved insuitable solvent. Our ion-selective electrode was prepared from the membrane formed by the evaporation of the solvent [20, 21].The electrode was filled with 0.1 M $NaSO_3$ and 0.1 M KCl. Membrane electrodes were held in the air when not in use.

Result and Discussion

The electrode performance of IS electrodes are highly depending on the conditions such as storage and their compositions. The criteria of a suitable ISE are specified with response time, repeatability, reproducibility, LOD and LOQ, linear working range and selectivity. The usage of ISE in real sample analysis finally proves the reliability of the proposed sensor against analyze in real conditions.

Effect of Membrane Composition

It is well known that the sensitivity, linear range and selectivity of the ISEs depend on the nature of the used carrier. In this study, membranes in 4 different quantities were prepared to identify the membrane composition effect. The responses of electrodes were measured at different sulphite ion concentrations changing between$1.0x10^{-7}$ and $1.0x10^{-1}$ M. Calibration curves are given in Fig. 1 for four different compositions of electrodes. The slope of the electrode having 5% PFOS, 40% PVC and 55% DBF (5% PFOS) was 58 ± 4 mV; the one with 1% PFOS, 40% PVC and 59% DBF (1% PFOS) was 31± 5 mV,3% PFOS, 40% PVC and 57% DBF(3% PFOS) was 41 ± 3, 7% PFOS, 40% PVC and 53% DBF (7% PFOS) was 43 ± 6 mV ($1.0x10^{-7}$ to $1.0x10^{-1}$ concentration range). Since membranes containing 5% PFOS, 40% PVC and 55% DBF (5% PFOS) have the highest slope, this membrane composition was determined in sulfite determination (Fig. 1 and Table-1).ISEs of the same composition were suspended in air when no measurement was made. Schematic representation of the electrode according to these data:

Ag, AgCl, KCl (sat.) ||sample | ISE |Ag(1)

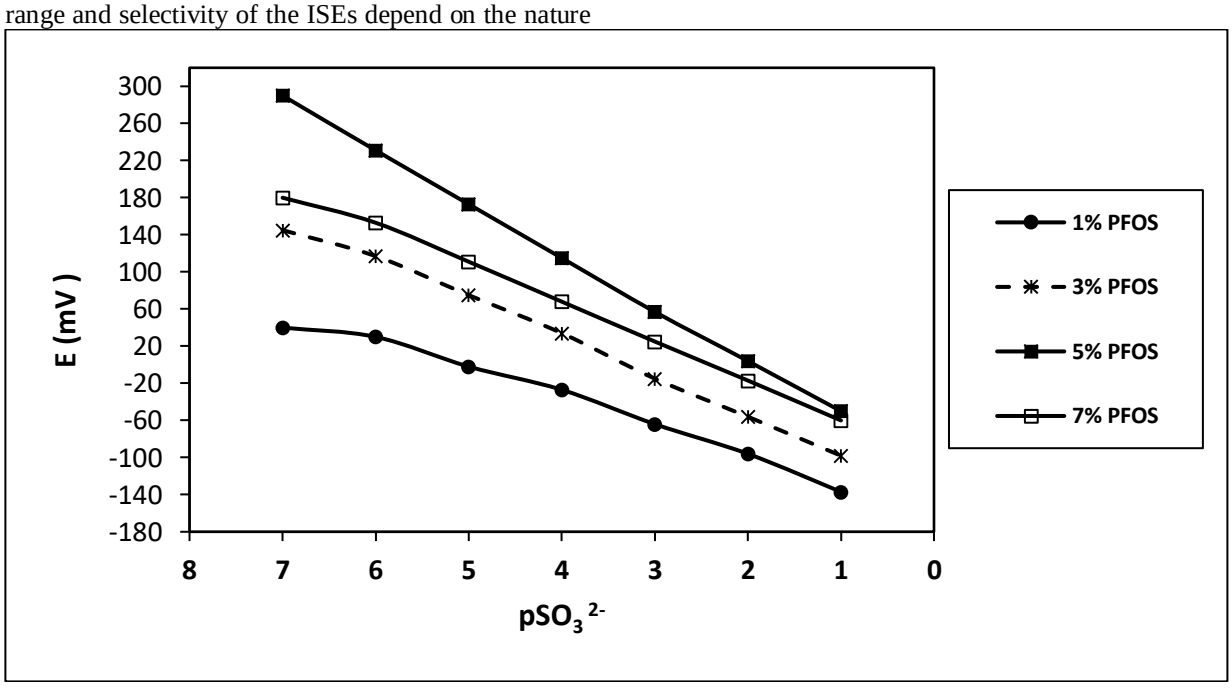

Fig. 1: Calibration curves for electrodes in different composition.

Table-1: Calculated slopes ($1.0.x10^{-7}$-$1.0x10^{-1}$) Mfor electrodes different composition. (N=5, 95% CI (confidenceinterval).

Composition	$CI = \bar{x} \pm \frac{t.s}{\sqrt{N}}$, mV	R^2	LOD (M)
1% PFOS (1% PFOS, 40% PVC and 59% DBF)	31.2 ± 5.1	0.9876	$7.8x10^{-8}$
3% PFOS (3% PFOS, 40% PVC and 57% DBF)	41.5 ± 3.4	0.9974	$5.6x10^{-8}$
5% PFOS (5% PFOS, 40% PVC and 55% DBF)	58.6 ± 4.3	0.9998	$1.2x10^{-8}$
7% PFOS (7% PFOS, 40% PVC and 53% DBF)	43.7 ± 6.5	0.9985	$4.4x10^{-8}$

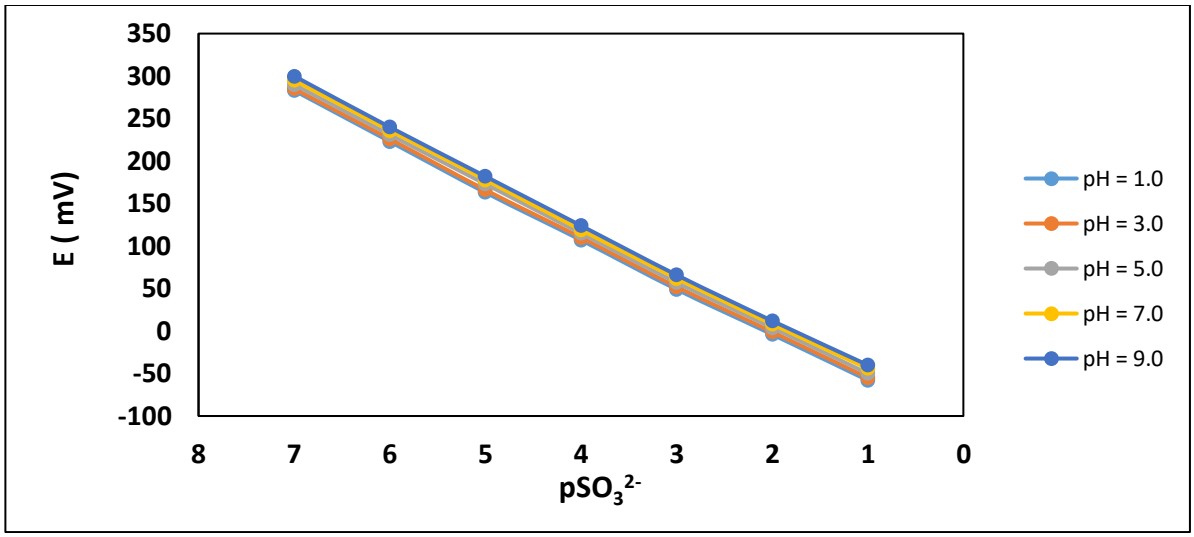

Fig.2: The change of potential with potassium ion concentrationat various pH values (membrane composition is 5% PFOS +40% PVC +55% DBF).

Effect of Membrane Thickness

In order to examine the effect of membrane thickness on ISE sensitivity, electrodes containing 5% PFOS, 40% PVC, 55% DBF were prepared in different weight amounts (0.3g and 0.4g). It was determined that the electrode with 0.3 g membrane mass had a short response time.

Effect of pH

Using some acidic or basic buffers and acidic or basic electrolytes, the pH of the medium was brought to the range of 1-9. Calibration graphs were obtained for the sulphite concentration of the electrode at each pH value. As can be seen from Fig. 2, the performance of the electrode was found to be quite good around pH 1-9.

Response time of electrodes

When sulphite concentration is changed from $1.0x10^{-7}$-$1.0x10^{-6}$ M, $1.0x10^{-6}$-$1.0x10^{-5}$ M, $1.0x10^{-5}$-$1.0x10^{-4}$ M, $1.0x10^{-4}$-$1.0x10^{-3}$ M, $1.0x10^{-3}$-$1.0x10^{-2}$ M and $1.0x10^{-2}$-$1.0x10^{-1}$ M, the response of electrode was found to be 30 seconds.

Selectivity Coefficient of ISE

The sensitivity of ISE to other anions and cations was examined ($K_{A,B}^{pot}$) [22].The change of potential for each addition of interfering ion are recorded Fig. 3 and Fig. 4.The selectivity coefficients of the electrode calculated against Na^+, K^+, NH_4^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Cr^{3+}, F^-, Cl^-, I^-,NO_3^-, S^{2-}, CO_3^{2-}, SO_4^{2-}, $PO_4^{3-}$are given in Table-2.

Table-2: Selectivity Co-Efficiencies, $K_{A,B}^{pot}$, for sulphite electrode in mixed solutions of some cations and anions (presence of 1.0 x 10^{-5} M SO_3^{2-}).

[a]B (Cations)	$K_{A,B}^{pot}$	[a]B (Anions)	$K_{A,B}^{pot}$
Na^+	$1.1x\ 10^{-3}$	F^-	$1.4x10^{-3}$
K^+	$1.2x\ 10^{-3}$	Cl^-	$1.2x10^{-3}$
NH_4^+	$1.4x\ 10^{-3}$	I^-	$1.1x10^{-3}$
Ca^{2+}	$1.8x\ 10^{-3}$	NO_3^-	$1.4x10^{-3}$
Cu^{2+}	$2.7x\ 10^{-3}$	S^{2-}	$2.4x10^{-3}$
Zn^{2+}	$1.9x\ 10^{-3}$	CO_3^{2-}	$1.5x10^{-3}$
Fe^{3+}	$3.0x\ 10^{-3}$	SO_4^{2-}	$1.7x10^{-3}$
Cr^{3+}	$2.9x\ 10^{-3}$	PO_4^{3-}	$2.0x10^{-3}$

[a]B : interfering ion; A: sulphite ion.

Determination of sulphite ion in dried apricot

Sulphite ion determination was made in dried apricot samples. Used as a preservative sulfite, manufactured in Turkey's Malatya and dried apricots in supermarkets samples were used. The same samples were analyzed by differential pulse polarography and results were compared in Table-3. The purpose of the case study is to test. t and F tests were applied to the values obtained from the analysis. Results were close to each other in both methods.

Table-3: Comparison of measured sulphite amount (µg/kg) in dried apricot samples by ISE and differential pulse polarographic (DP Polarography) method 95% confidence interval and N=5.

Parameters	ISE	DP Polarography
Found (mg/kg)	2.328 ± 0.2417	2.521 ± 0.2785
LOD (M)	$1.2x10^{-8}$	$6.5x10^{-6}$
RSD (%)	0.76	1.33
t-test ($t_{critical}$ =3.18)	1.47	2.94
F-test ($F_{critical}$ = 9.28)	5.48	7.18

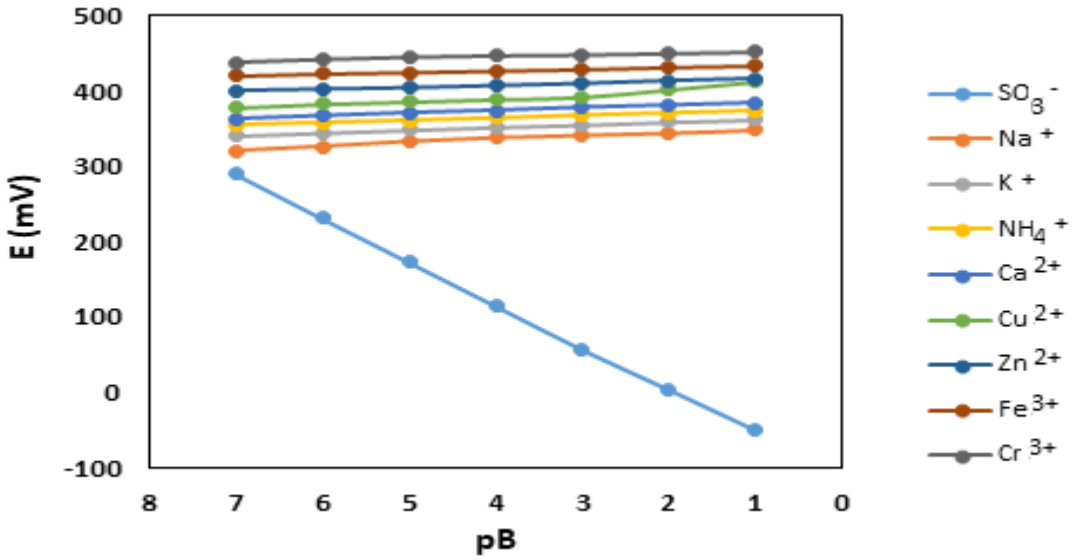

Fig. 3: The response of the potassium electrode against somecations.

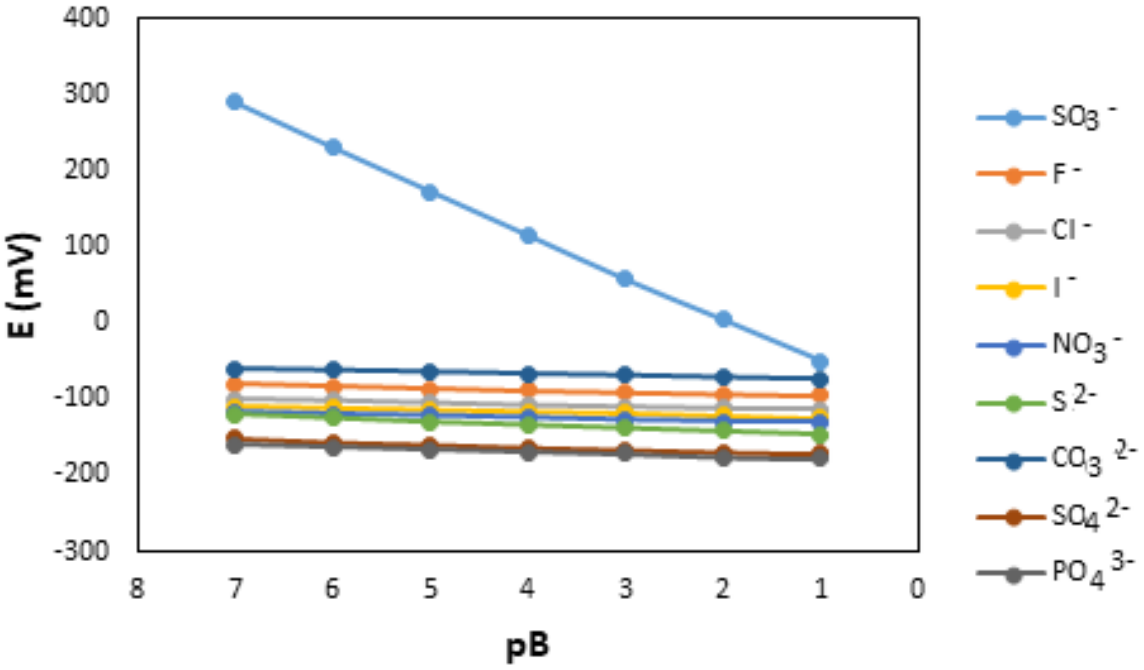

Fig. 4: The response of the potassium electrode against some anions.

Conclusion

In this work, an electrode capable of determining sulphite directly was developed for the first time. The slope of the linear part of this ISE ($1.0x10^{-7}$-$1.0x10^{-1}$ M) was 58 ± 4 mV per 10-fold change in sulpfite ion. This ISE does not show selectivity to ions such as Na^+, K^+, NH_4^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Cr^{3+}, F^-, I^-, NO_3^-, S2-, CO_3^{2-}, SO_4^{2-}. When used 5 times a day, the life of the electrode was found to be approximately 210 days. It was possible to determine the amount of sulfite ions in dried apricots. Preparation of the electrode is simple; it performs very well in terms of reproducibility, precision and long life.

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