The International Journal of Engineering and Science (IJES)
|| Volume || 14 || Issue 12 || December || Pages || PP 435-438 || 2025 ||
ISSN (e): 2319 – 1813 ISSN (p): 2319 – 1805

Investigation of sulfite content in fresh apricots sold in markets using ion selective electrodes

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----------ABSTRACT----------
A polymer-based ion-selective electrode composed of 5% perfluorooctane sulfonic acid (PFOS), 40% poly vinyl chloride (PVC), and 55% dibutyl phthalate (DBF) was prepared as the sulfite ion sensitive electrode.This electrode was measured to be sensitive to a 0.1 M sulfide concentration of $1x10^{-7}$ with a slope of approximately 58 mV.This electrode has a response time of 30 seconds and allows for operation over a wide pH range from 1 to 10. Furthermore, the sulfide electrode showed no sensitivity to other anions and cations. the life of the electrode was found to be approximately 210 days. With this electrode, 5 different fresh apricot samples sold in markets in Ankara were taken and solubilized by the wet combustion method.The analytical performance values of the sulfide electrode were measured using synthetic samples.To measure sulfites, samples were immersed in 0.1 M acetic acid/acetate buffer (pH 4.0) for approximately 10 minutes.Sulfide contents in these fresh apricot samples were determined to range from 3.25 to 3.91 mg/kg using a sulfite electrode. The same samples were also measured by ion chromatography. The results were found to be consistent.

KEYWORDS; Sulfite, ion selective electrode, ion chromatography, fresh apricots.

Date of Submission: 13-12-2025 Date of acceptance: 28-12-2025

I. INTRODUCTION

Sulfite determination plays an important role due to its use as a preservative in some food products. It is a known fact that high sulfite levels in food can cause certain health problems [1-2]. Determining the amount of sulfites in wastewater from the food industry has also become important. In a study conducted on workers employed during the apricot sulfur treatment season in Malatya, it was found that inhaling SO2 caused various asthma diseases [3]. High concentrations of direct sulfite and total sulfite were detected in serum samples taken from individuals exposed to SO2. In recent years, it has been found that consuming sulfur-containing foods causes asthma and deaths [4]. The US Food and Drug Administration has requested that sulfite levels in food exceeding 10 ppm be declared [5]. The most common methods for sulfite determination include iodometric titration [6], spectrophotometric methods [7-8], high-performance liquid chromatography (HPLC) [9], FIA-CL [10-11] and some electrochemical methods [12-14]. These methods are expensive and time-consuming to analyze.

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]. In this study, a membrane-based sulfide electrode, which is easy to prepare, has a short analysis time, and high sensitivity, was used for the determination [16]. The sulfite content of fresh apricot samples from Turkish markets was analyzed using a specially prepared sulfite-selective electrode. Ion chromatography was also performed on the same samples, and the results were found to be consistent.

1.1 Apricot nutritional value

Apricots are a fruit that has positive effects on human health due to the organic and inorganic substances they contain. Apricots contain high amounts of sugar, starch, protein, pectin, pectose, cellulose, organic substances, vitamins A, B, B_2, C, E, P, PP, folic acid, small amounts of K_2O, CO_3, P_2O_5, CO, even smaller amounts of Na_2O, CaO, MgO, Fe_2O_3, and trace amounts of Zn, A1, and Cu. Apricots are very rich in potassium and the vitamin beta-carotene. Vitamin A is essential for the health of the epithelial tissue covering the body and organs, the health of the eyes, the development and health of bones and teeth, and the functioning of the endocrine glands. 200-250 grams of apricots in a diet containing sufficient fat can meet 1/3 of the daily vitamin A intake. Furthermore, the fact that apricots are low in sodium and high in potassium can be helpful in regulating certain special diets.

Nutritional Values per 100 grams (1)

Dried apricots

188 calories

Carbohydrates 87% **Protein 10%** **Fat 3%**

	Amount	GRD %
Total Fat	**0.7g**	**1%**
Sodium	**56mg**	**%2**
Total Carbohydrates	**51.1g**	**19%**
Total sugar	43.4g	
Fiber	7.7g	27%
Net Carbohydrate	43.4g	
Protein	**4.8g**	**10%**

Vitamin	Amount	GRD %
B3 (Niacin)	3mg	19%
B2 (Riboflavin)	0.2 mg	15%
B5 (Pantothenate)	0.7 mg	14%
B6 (Pyridoxine)	0.2 mg	10%
A (RAE)	53.8µg	6%
B9 (Folate)	14µg	4%

Mineral	Amount	GRD %
Copper	0.4 mg	44%
Potassium	1.880mg	40%
Iron	4.1 mg	23%
Manganese	0.4 mg	17%
Magnesium	65mg	15%
Selenium	7µg	13%
Phosphorus	120mg	10%
Calcium	92mg	7%
Zinc	0.7 mg	6%
Chloride	35mg	%2

Schema 1: Nutritional value of dried apricots

II. MATERIAL AND METHODS

2.1 ***Reagents and apparatus***

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, PVC, DBF and other reagents are Sigma-Aldrich. For potential measurements, Orion Star A214 pH/ISE Benchtop meter, reference electrode and IKA Plate magnetic stirrer mixer were used.

2.2 Preparing Membrane Electrode

A mixture of 5% PFOS, 40% PVC and 55% DBF plasticizer, with a total mass of 0.3 g, was dissolved in suitable solvent. Our ion-selective electrode was prepared from the membrane formed by the evaporation of the solvent [17-18]. 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 [16].

III. RESULT VIEW

3.1 Electrode sensitivity

A sulfite-sensitive electrode was prepared with a composition of 5% PFOS, 40% PVC, and 55% DBF, resulting in a total membrane mass of 0.3 g. The electrode was conditioned by incubating it overnight in a $1x10^{-5}$ M sulfite solution. 0.1 M Acetic acid/acetate buffer (pH=4.0) support electrolyte was added to the cell. The sulfite electrode and the Ag/AgCl reference electrode were placed, and the potential of the support electrolyte was recorded. Sulfite concentrations were increased tenfold within the cell, and constant potential values were recorded. Potential values in relation to sulfite concentration are given in Figure 1.

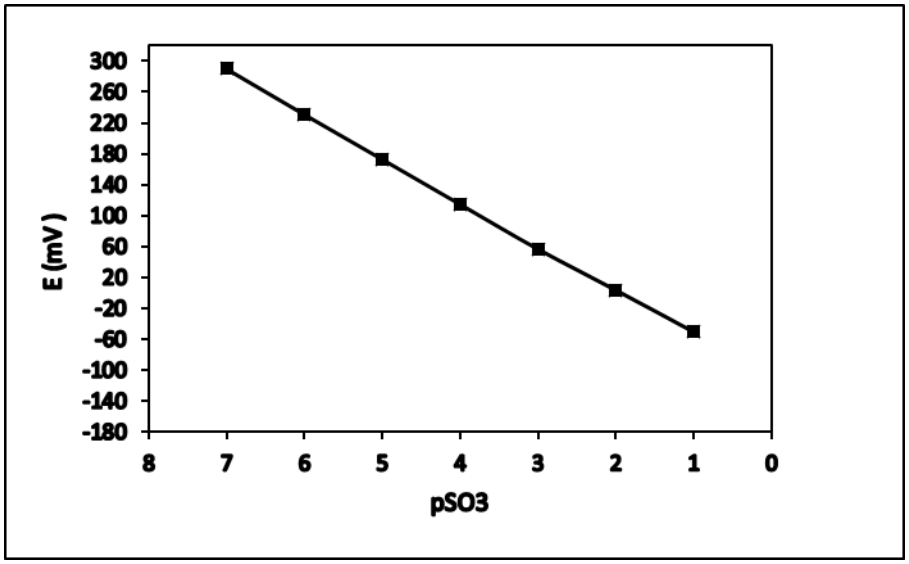

Figure 1: Calibration graph against sulfite concentration.

According to our measurement from this graph, the electrode slope was measured as 58 ± 4 mV for a sulfide concentration of 0.1 M with a slope of 1 x 10^{-7} M, and this result indicates that our electrode is compliant with the Nernst Equation.Furthermore, it was determined that the electrode's response time was 30 seconds, its sensitivity did not change between pH 1 and 10, and it had no interference effect with other anions and cations. the life of the electrode was found to be approximately 210 days [16].

3.2 Removing sulfites from apricots

Samples of apricots were taken from five different large supermarkets in Ankara. These were labeled A, B, C, D, and E, respectively. Approximately 0.5 g of each apricot sample was weighed. To measure the sulfite content, each sample was placed in 50 ml of 0.1 M acetic acid/acetate buffer solution (pH=4.0) and left for 10 minutes. The sulfite concentrations that passed into the solution were prepared for measurement.

3.3 Sulfide levels in apricot samples

Fresh apricot samples were first measured using a sulfite electrode in 0.1 M acetic acid/acetate buffer (pH=4.0). Then, the same samples were analyzed using ion chromatography. The analysis results are given in Table 1. T-tests and f-tests were applied to the results of both methods. The results were found to be in agreement.

Table I. Sulfite levels in samples of fresh apricots found in markets.

Sample	Sulphite electrode	Ion Chromatography	t-test ($t_{critical}$ =3.18)	F-test ($F_{critical}$ = 9.28)
A	3.15 ± 0.1 4	3.12 ± 0.15	1.65	5.21
B	3.29 ± 0.17	3.31 ± 0.16	1.74	5.42
C	3.37 ± 0.22	3.36 ± 0.17	1.81	5.64
D	3.31 ± 0.1 9	3.32 ± 0.14	1.75	5.48
E	3.55 ± 0.23	3.57 ± 0.24	1.92	5.91

IV. CONCLUSION

In the food industry, sulfites are used as preservatives because their addition to various foods (vegetables, fruits, and beverages) prevents oxidation. They inhibit bacterial growth and help preserve vitamin C. For sulfite quantity determination, a prominent analytical method in the food sector, an ion-selective electrode was proposed. The electrode prepared for this purpose showed a slope of approximately 58 mV against sulfite concentration. Its short response time and ability to operate over a wide pH range were significant advantages. Samples of fresh apricots obtained from markets in Ankara were placed in 0.1 M acetic acid/acetate buffer. Sulfide concentrations in these solutions were determined both using the ion-selective electrode and by ion chromatography. The results were found to be consistent with each other.

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