



Novel pararosaniline based optical sensor for the determination of sulfite in food extracts

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ABSTRACT

Sulfite, which is a protective agent in various food industries, also is known as an allergen. Therefore, sulfite content in food must be monitored and controlled. In this context, a novel optical sensor is designed for simple, rapid and sensitive determination of the sulfite content in food samples. Acidified pararosaniline (PRA) hydrochloride reagent in cationic form was immobilized on the surface of the Nafion cation exchanger membrane by electrostatic interactions. In formaldehyde medium, the pale purple PRA-Nafion film was converted to rich purple due to the highly conjugated alkyl amino sulfonic acid formation in the presence of sulfite and the absorbance change at 588 nm was recorded. The proposed optical sensor gave a linear response in a wide concentration range for sulfite. The limit of detection (LOD) and the limit of quantification (LOQ) values obtained for sulfite were 0.084 and 0.280 ppm SO₂ equivalent, respectively. The proposed optical sensor was validated in terms of linearity, additivity, precision and recovery parameters. The sulfite contents obtained for real food extracts were found to be comparable to the conventional iodometric titration results (with the exception of highly colored samples containing reducing agents, where iodometry was shown to exhibit a systematic error while the proposed sensor could measure the true value). The proposed optical sensor is insensitive to positive interferences from turbidity and colored components of the sample. Sulfite determination in a complex food matrix can be performed using the rapid, simple and sensitive PRA-based sensor without a need for pre-treatment.

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1. Introduction

The term sulfite is used to describe tetravalent sulfur-based materials such as sulfites, sulfur dioxides, bisulfites, and metabisulfites, which are commonly used in a variety of foods and beverages. In order to prevent bacterial growth and oxidation, as well as to control both enzymatic and nonenzymatic reactions that may occur during production and storage processes, sulfites as antibacterial and antioxidizing additives are often used [1]. In the food industry, sulfites play a role as preservatives, especially in beverages, and syrups that require low pH values where sulfites are converted into a powerful antimicrobial agent, sulfurous acid. Besides, sulfites are also used to prevent undesired browning in fruits and vegetables, in the dough as a conditioner, to bleach certain food starches and cherries [2–4]. In addition, sulfites are used to preserve the stability and effectiveness of certain drugs [5]. On the other hand, it is known that high concentrations of sulfite cause

allergic reactions in sensitive consumers. The US Food and Drug Administration recommends warning labels be contained on solid foods containing more than 10 mg/kg sulfite, and beverages containing more than 10 mg/L sulfite [6,7]. Moreover, the high sulfite contents of exported fruits and vegetables should be subject to “food alert notifications” based on the general principles and requirements of food law valid in the European Community member countries [4]. Thus, sulfite content should be closely monitored in food.

In recent years, there has been a growing interest in optical sensors that are sensitive and selective to target analytes as a result of various physico-chemical reactions [8,9]. Because of their low cost, short analysis time, small size and suitability for on site/*in situ* analysis, optical sensors show superiority over classical instrumental methods. Reagent based sensors, called optrodes, can be applied to simple, rapid and low-cost analyses, and can also be readily converted to test kits or test strips, making them suitable for *in situ* tasks [10,11]. Optrodes are usually produced by immobilizing various reagents on suitable membrane surfaces [12] by applying techniques such as covalent bonding, electrostatic interaction, and incorporation into the membrane [13]. Being a perfluorosulfonate

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cation exchanger membrane, Nafion is transparent, stable, and has hydrophilic and hydrophobic regions. The hydrophilic region provides cation selectivity and ionic conductivity, while the hydrophobic region contains the basic chains. There is also an interlayer region between hydrophilic and hydrophobic regions [14,15]. In recent years, Nafion has been used as a support material in the design of metal ion, pH, and oxygen sensors [16]. In addition, our laboratory has used Nafion as a support material in devising novel optical sensors for total antioxidant capacity measurement [17–19].

A most common method for determining sulfite in food is Monier-Williams method [20], in which the sample is distilled under acidic conditions and the end-point titration is performed. But this method is time-consuming due to the distillation process and is unsuitable for low sulfite concentrations. Another common method, iodometric titration using a starch indicator [21], has sensitivity problems. Recently, alternative and effective instrumental techniques, such as flow injection analysis (FIA) [22], chemiluminescence [23], anodic stripping voltammetry [24], ion chromatography [25], and high performance liquid chromatography [26] have been reported. These methods have disadvantages such as reagent consumption at high volumes, long analysis time and need for sophisticated instrumental infrastructure. The pararosaniline (PRA) method used for the detection of SO_2 in the atmosphere [27] has recently been tried to make it suitable for sulfite determination in food samples and to attain lower analysis times with modification studies. In this method, highly conjugated amine salt and pararosaniline hydrochloride (a component of the “basic fuchsin” dye) are used to determine free sulfites. When hydrochloric acid and formaldehyde (FA) are added to aqueous pararosaniline, the light purple color darkens upon exposure to sulfite. This method can be used as a quantitative test for sulfites. Li and Zhao were able to detect the sulfite level semi-quantitatively in 5 min with the modification they made in the method. After waiting for 10 min at room temperature, more accurate results were obtained with absorbance measurements [28]. Almeida and co-workers designed a flow-batch analyzer (FBA) associated with digital images (DIs) obtained from a webcam to measure the amount of sulfite in vinegar samples [29]. Monro and co-workers proposed a dip sensing platform for the detection of free sulfur dioxide in wine, based on a colorimetric technique placed in a microstructured optical fiber [30].

Based on the usage of PRA method of sulfite determination, we developed an optical sensor applicable to the determination of sulfite content of complex samples, which, to the best of our knowledge, is the first colorimetric sulfite sensor to serve this purpose in food extracts. The acidified cationic PRA reagent was electrostatically immobilized onto the anionic sulfonate groups of unmodified Nafion membrane surface. The proposed optical sensor has been successfully applied to standard sulfite solutions, food extracts, and beverages, and the results were compared with those of traditional iodometric titration. The proposed method has certain superiorities over classical methods such as operation in turbid solutions, unresponsiveness to intrinsic color interference from the sample, reagent saving and on site/in situ analysis capability.

2. Experimental

2.1. Chemicals and equipment

The following chemical substances of analytical reagent grade were supplied from the corresponding sources: Pararosaniline hydrochloride (PRA), ethanol (EtOH), sodium thiosulfate, starch, Sigma-Aldrich; Nafion® 115 perfluorinated membrane (thickness 0.005 in), Aldrich; hydrochloric acid (HCl), potassium iodide (KI), Riedel-de Haën; sodium sulfite (Na_2SO_3), formaldehyde (FA), iodine

(I_2), Merck. Wines, vinegar, and apricots samples were supplied from local markets. A certified reference sample (CRM) of dried apricot containing 1478 mg/kg SO_2 was obtained from the Metrological Institute of the Scientific and Technological Research Council of Turkey (TUBITAK).

The visible spectra and absorption measurements were recorded using a Varian Cary Bio 100 UV–vis spectrophotometer. Quartz cuvettes with 2 mm path length for the sensor were used for absorbance measurement with the sensor. A Scientz JY88-IIN ultrasonic extraction system was used for preparing apricot extracts. Other related apparatus and accessories were Biosan Programmable rotator-mixer Bulti Bio RS-24 and Elektromag vortex stirrer.

2.2. Preparation of solutions

PRA stock solution (2.6×10^{-3} M) was prepared by dissolving pararosaniline hydrochloride in 10% aqueous ethanol solution and was stored at 4 °C. Sodium sulfite solution was freshly prepared in water. Acidified PRA reagent for optical sensor manufacture was prepared by adding 1 mL of PRA stock solution and 0.28 mL of 37% HCl solution into a 100 mL volumetric flask, diluting with deionized water and completing to the mark. The CRM was prepared in accordance with the instructions for use in analysis. The sample was stored at –80 °C prior to analysis. The CRM was allowed to dissolve for one night at +4 °C the day before the analysis. The package was allowed to warm to room temperature for 1 h before opening. After the package was opened, it was homogenized by mixing with a spatula. The CRM and apricot extracts were obtained using ultrasonic extraction technique at 20 kHz and output power of 650 W for 15 min. Each of the wine and vinegar samples were diluted with water to the appropriate volumes for analysis.

2.3. Sensor fabrication

Nafion membrane was sliced into 4.5×0.5 cm pieces, immersed into a tube containing 9 mL of acidified PRA reagent, and agitated for 25 min in a rotator. The Nafion loaded with the PRA reagent was called the ‘blank sensor’, and its color was pale yellow.

2.4. PRA-based optical sensor method

The blank sensor was placed in a tube containing working solution (40 μL of FA + 2 mL of 1 M HCl + (6.96 mL – x) mL of water) and agitated for 10 min in a rotator. Then, a further 10 min of agitation was applied to the solution by adding x mL of sample solution to enable color development. The colored membrane was taken out and placed in a 2 mm optical cuvette containing working solution (to prevent the color change of slices in the cuvette), and its absorbance at 588 nm was read against a reference membrane prepared under identical conditions without sample.

2.5. Iodometric titration method

Iodometric titration was used as the reference method for the determination of the amount of sulfite [21]. Back titration was used to prevent sulfite loss in free SO_2 form in an acidic medium.

2.6. Interference studies

The interference effects of 10-fold (as ppm/ppm) concomitant species commonly found in food extracts and beverages to the determination of 5 ppm sulfite in a solution using PRA-based optical sensor method were studied.

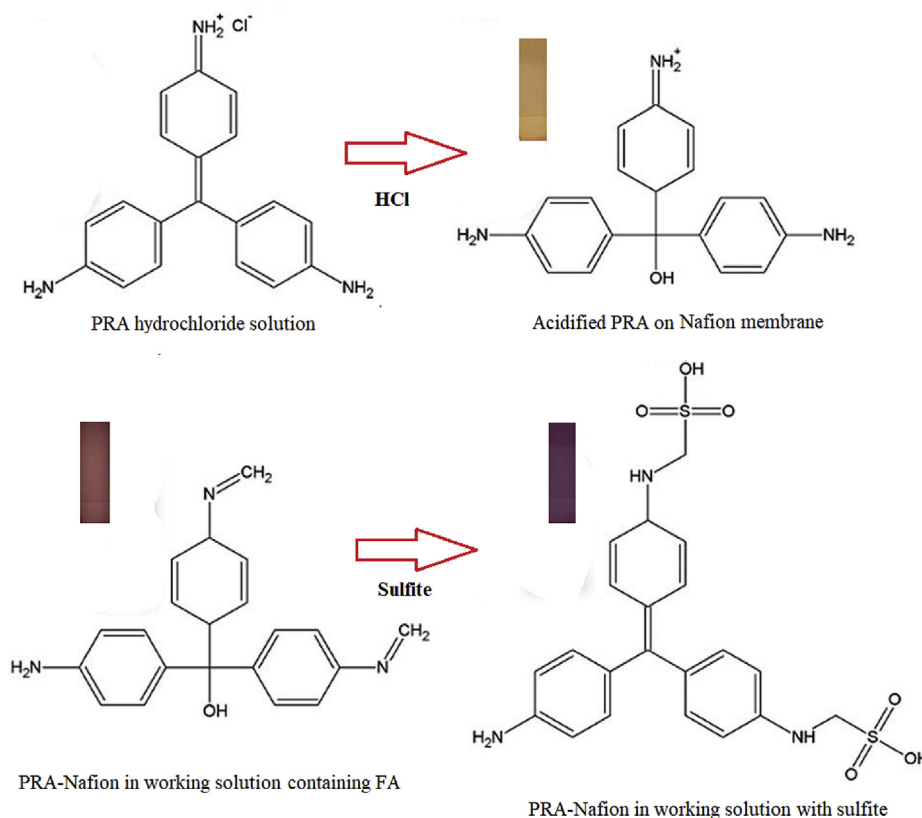


Fig. 1. The schematic lay up for optical sensor preparation and sulfite detection (FA: formaldehyde, PRA: pararosanine).

2.7. Statistical analysis

Statistical analyses were made with the use of Excel software (Microsoft Office 2016) for obtaining the mean along with standard error. Results were expressed as the mean $\pm$ standard deviation (SD). Using SPSS software for Windows (version 13), the data were evaluated by two-way analysis of variance (ANOVA).

3. Results and discussion

The PRA hydrochloride aqueous solution is bright magenta. The acidified solution with hydrochloric acid is bleached to give a pale yellow color in cationic form. In the production of the designed optical sensor, the acidified pale yellow cationic complex is immobilized on the membrane surface as a result of electrostatic interactions through anionic sulfonate groups of Nafion. The resulting pale yellow blank sensor is immersed in an acidic solution (working solution) containing FA before the analysis and a pale purple color is formed depending on the iminium ion formed on the sensor surface. Then the sulfite-containing solution is added to the medium (sulfite reacts as H_2SO_3 due to the acidity of the medium, as the working pH was well below the first pK_a value of sulfurous acid) and a highly conjugated alkyl amino sulfonic acid is formed, and the sensor membrane surface attains a rich purple color (Fig. 1). This stable color on Nafion after reaction of acidified PRA with FA and sulfite is not detached from the membrane surface although the adsorbate contains anionic sulfonate groups because dyes immobilize to cation exchange membranes not only by ion exchange but by a combination of electrostatic and hydrophobic interactions [31]. As a result, the absorbance of the rich purple colored sensor at a wavelength of 588 nm is measured (Fig. 2).

3.1. Analytical figures of merit

The linear equation of the calibration graph obtained for sulfite using the proposed optical sensor was found to be $A_{588} = 0.062C + 0.0173$ ($r = 0.996$) (Fig. 3). In the equation, A denotes absorbance (measured against PRA-Nafion in working solution (reference sensor)) and C symbolizes concentration in ppm (or microgram per milliliter). The detection and quantification limits (LOD and LOQ) for sulfite were found as 0.084 and 0.280 ppm, respectively. The absorbance values for sulfite in the range of 0.32 to 19.08 ppm (as final concentration) showed a linear correlation. An excellent linear response was obtained in a wide concentration range with the developed optical sensor as an unexpected case in

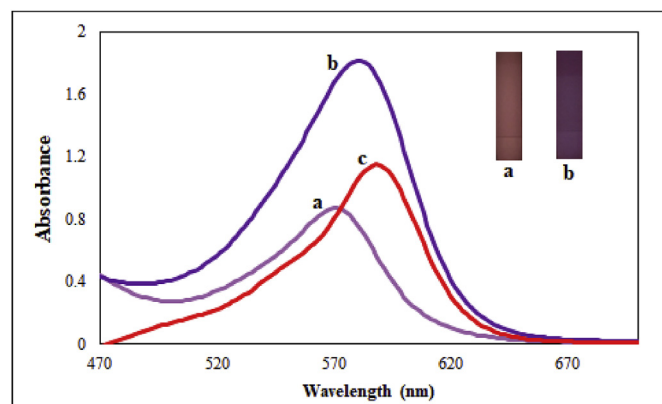


Fig. 2. Visible spectra of (a) PRA-Nafion in working solution (reference sensor) against working solution, (b) PRA-Nafion in working solution with sulfite against the working solution, (c) PRA-nafion in working solution with sulfite against reference sensor.

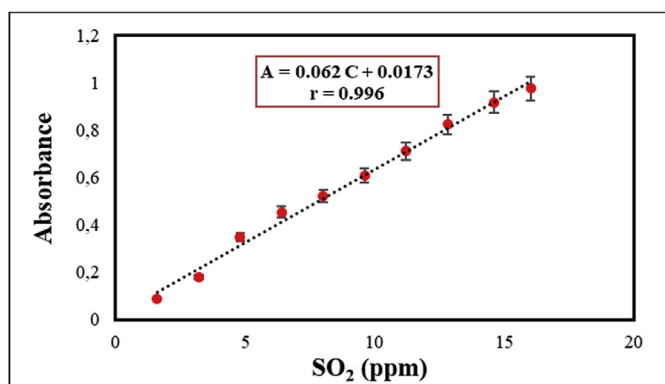


Fig. 3. The calibration curve of sulfite (as absorbance versus concentration) with respect to the PRA-based optical sensor ($N = 3$).

solid colorimetric sensors. The standard calibration curve of sulfite was redrawn in red wine. The linear curves of sulfite standard in pure water and in real complex matrix, such as red wine, showed an excellent parallelism (Fig. 4). Thus, it was observed that there was no chemical interaction between the analyte and red wine constituents (that would otherwise cause chemical deviations from Beer Law) and that the absorbances for sulfite were additive.

Known amounts of sulfite standards (3.2, 6.4, and 9.6 ppm) were added to the diluted red wine sample and the amount of sulfite in this solution was determined using the developed sensor to investigate the precision and recovery of the method (Table 1). The relative standard deviation (R.S.D., %), which is an indicator of the precision of the method, was found to be 6.05% at a concentration of 9.60 ppm SO_2 , which is the highest in the studied concentration range. The sulfite recoveries ranged between 96.5% and 105.6% with the developed optical sensor. The original sulfite concentration of the diluted red wine sample was determined as 3.15 ppm SO_2 . This was confirmed with the reference standard method of iodometry as 3.68 ppm SO_2 .

3.2. Interferences

The possible interference effects of 10-fold (as ppm/ppm) interferent compounds commonly found in food matrix on the determination of 5 ppm SO_2 equivalent sulfite with the PRA-based optical sensor are shown in Table 2. The presence of 10-fold Cu^{2+} , Fe^{3+} , Cr^{3+} , thiosulfate, oxalate, tartrate, citrate interferents that may be found in beverages and food extracts did not interfere with the proposed PRA-based optical sensor (as evaluated by the change of sulfite absorbance signal by less than $\pm 5\%$). These potential

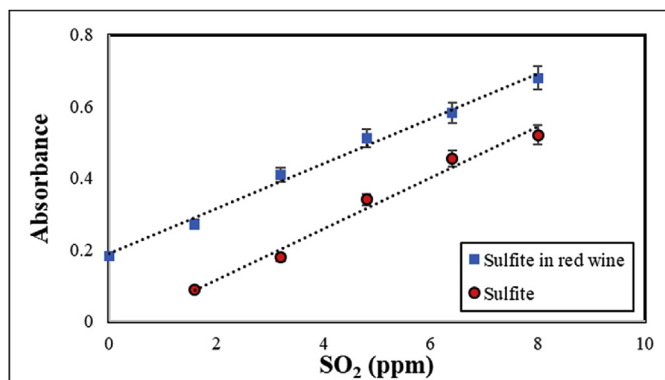


Fig. 4. Calibration curves of sulfite alone and in red wine with respect to the PRA-based optical sensor ($N = 3$).

Table 1

Precision and recovery of the developed PRA-based optical sensor.

Sulfite additions to a red wine sample	
Added conc. (SO_2 eqv., ppm)	3.20
Mean (SO_2 eqv., ppm) ^a	3.38
S.D. ^b	0.13
R.S.D., % ^c	3.85
REC, % ^d	105.6
Added conc. (SO_2 eqv., ppm)	6.40
Mean (SO_2 eqv., ppm) ^a	6.25
S.D. ^b	0.35
R.S.D., % ^c	5.60
REC, % ^d	97.7
Added conc. (SO_2 eqv., ppm)	6.40
Mean (SO_2 eqv., ppm) ^a	6.25
S.D. ^b	0.35
R.S.D., % ^c	5.60
REC, % ^d	97.7

Sulfite concentration of unspiked (but diluted) red wine sample was 3.15 ppm SO_2 . Mean and recovery (%) were calculated based on the concentration of added sulfite.

^a Mean.

^b Standard Deviation.

^c Relative Standard Deviation.

^d Recovery.

interferents were recommended to be investigated for sulfite determination in other literature sources [28,29].

3.3. Sulfite content measurement of real samples

The sulfite contents of the tested food extracts and beverages were determined as ppm SO_2 equivalents by using the proposed sensor and conventional iodometric titration method, as summarized in Table 3. The results obtained by both methods were compatible with each other at 95% confidence level ($P = 0.05$, $F_{\text{exp}} = 3.472$, $F_{\text{crit}}(\text{table}) = 5.987$, $F_{\text{exp}} < F_{\text{crit}}(\text{table})$). In addition, there was a reasonable agreement between the ppm SO_2 values found by the proposed PRA-based optical sensor and those of the conventional iodometric titration method, with a correlation coefficient of $r = 0.9924$. This is a strong positive correlation ($N = 7$ and $r^2 = 0.9849$) at $P < 0.001$ level, showing that the result is highly significant. White vinegar showed the highest sulfite content while apple vinegar showed the lowest sulfite content among studied liquid samples for both methods. The sulfite content of CRM of dried apricot was determined as 1524 ± 52 mg/kg SO_2 ($n = 3$) by the proposed PRA-based optical sensor. The determined sulfite content was only 3% higher than the reference value (1478 mg/kg SO_2), confirming the absence of any bias based on equivalence with CRM assigned values.

The higher sulfite contents were obtained for colored samples using the conventional iodometric method, as compared with the proposed optical sensor. Some reducing compounds and coloring

Table 2

Effects of various possible interferents in food matrix to the proposed PRA-based optical sensor in the determination of 5 ppm SO_2 equivalent sulfite in solution.

Interferents	Interferent/Sulfite ratio	Presence (+) or absence (–) of interference with the PRA-based optical sensor
Cu^{2+}	10	–
Fe^{3+}	10	–
Mg^{2+}	10	–
Cr^{3+}	10	–
Thiosulfate	10	–
Oxalate	10	–
Tartrate	10	–
Citrate	10	–
Acetic acid	10	–

Table 3

Sulfite content of some liquid samples and food extracts as assayed by the proposed PRA-based optical sensor and conventional iodometric titration method (N = 3).

Liquid Samples	PRA optical sensor (ppm SO ₂)	Iodometric titration (ppm SO ₂)
Red wine	45.05 ± 1.76	53.86 ± 2.28
White wine	37.53 ± 0.66	39.28 ± 1.90
White vinegar	53.34 ± 1.08	54.07 ± 1.32
Apple vinegar	19.46 ± 1.25	19.64 ± 1.09
Grape vinegar	35.51 ± 1.37	40.56 ± 2.20
Food Extracts	PRA optical sensor (ppm SO ₂)	Iodometric titration (ppm SO ₂)
Apricot extract 1	1.23 ± 0.04	1.21 ± 0.03
Apricot extract 2	0.83 ± 0.08	0.88 ± 0.01

(P = 0.05, F_{exp} = 3.472, F_{crit(table)} = 5.987, F_{exp} < F_{crit(table)})

agents in red wines are known to interfere with iodometric sulfite determination. For example, in an inter-laboratory comparison study according to a specified version of the Ripper iodometric titration for total sulfur dioxide, it was demonstrated that, although rapid and convenient, the Ripper method was severely limited by poor precision and large systematic error (amounting to 15–16%) in the determination of SO₂ in wine samples containing colored components and other reducing agents besides sulfite [32]. Additionally, there are difficulties with the determination of the titration end-point for red colored samples [33–35]. The method described by Almeida and co-workers requires a flow-batch analyzer in association with digital images (obtained from a web-cam) for the determination of sulfites [29]. On the other hand, the proposed optical sensor performs a sensitive sulfite assessment without the need for any sophisticated system and it has the potential to be converted to a kit format (similar to commercial pH indicator strips). The measurement made by Almeida et al. (i.e., with the aid of the calibration curve using the 'green channel' due to the fact that 'green' is the color component absorbed by the pale purple PRA-sulfite complex, and expected to yield the best response for absorbance calculation) [29] has a higher intercept and LOQ value than the proposed sensor and therefore has lower sensitivity. In addition, the proposed sensor is insensitive to positive interferences from turbidity and colored components frequently encountered in food samples.

4. Conclusions

In this study, a sensitive and selective optical sensor was designed for the determination of sulfite content in complex food matrices by visiting an old concept of pararosaniline colorimetry and bringing it a new life. The support material of the sensor is a Nafion cation exchanger membrane which is commercially accessible and is frequently used in optical sensor applications. The cationic form of PRA, which is a component of Basic fuchsin dye, in strong acidic medium is easily immobilized on the surface of the Nafion membrane by electrostatic interactions. The pale purple color of PRA-Nafion membrane in formaldehyde-containing working solution was intensified with sulfite, and the absorbance change associated with the formation of the rich purple highly conjugated alkyl amino sulfonic acid as a result of reaction with sulfite was measured at 588 nm. This colorimetric sensor was successfully applied to standard sulfite solution, beverages, and food extracts. The data obtained are given as ppm SO₂ equivalent. The proposed optical sensor is insensitive to positive interferences from turbidity and colored components frequently encountered in food samples. This simple, rapid and sensitive sulfite sensor can easily and precisely detect the critical limits of sulfite additions to fumigated dried apricot or wine (the maximum levels of sulfite contents of fumigated dried apricot and wine expressed as 2000 mg/kg and 200 mg/L SO₂ were set by the Commission Regulation (EU) [36]), whereas the 0.280 ppm SO₂ equivalent LOQ

obtained by this method was well below all legally set limits for food. In addition, this proposed optical sensor has the potential to be converted to a kit format (similar to commercial pH indicator strips).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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