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Fabrication of an Automatic Analyzer Based on an Integrated Gas Diffusion System and Optical Sensor for the Determination of Sulfite in Beverages and Dried Fruits

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ABSTRACT

Sulfite compounds are frequently utilized as antibacterial agents in the production of foods and beverages; however, they have the potential to cause allergic reactions in some individuals. In this work, a miniaturized automatic analyzer based on the integration of a microflow gas diffusion unit (GDU) with an optical sensor was developed. The GDU was microfabricated from polymethyl methacrylate (PMMA). In the donor stream of GDU, sulfite was reacted with HCl to produce sulfur dioxide gas (SO_2), which was then diffused through a PTFE hydrophobic membrane into a receiver segment holding Fe(III) and the colorimetric agent (1,10-phenanthroline). The released SO_2 gas reduced Fe(III) to Fe(II) and the resulting Fe(II)-phenanthroline complex was optically detected by a laboratory-made optical sensor. The automated system permitted the evaluation of sulfite amount in mg L^{-1} (SO_2). The non-linear calibration graph was obtained in the range of 1.0-35.0 mg L^{-1} (R^2 = 0.9991) with the limit of detection (3σ) down to 0.3 mg L^{-1}. The developed system offers greater levels of automation and user-friendliness and demonstrates adequate applicability for the determination of sulfite in fruit and beverage drinks samples from a local market of Thailand.

Keywords: Automation; Colorimetry; Gas diffusion unit; Microflow; Optical sensor

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1. Introduction

Sulfites (E220-E228) are commonly used as additives in juice and dried fruit processing to avoid microbiological spoilage and to retain color, browning, and oxidation. However, consuming foods containing high levels of sulfites can trigger allergies among sensitive consumers, with asthma and shortness of breath as possible symptoms. The assessment of preservatives is critical for regulation and consumer safety. Food and Drug Administrations (FDAs) of many countries have regulations for SO_2 used in foods and beverages; and it has been prohibited in fresh fruits and vegetables [1]. Under EU allergen labelling, sulfites at concentrations exceeding 10 mg kg^{-1} or mg L^{-1} should be labeled. Other countries, including the USA, Canada, Korea, and Thailand, mandate a warning label on food products containing 10 mg kg^{-1} sulfites [2]. Sulfite (expressed as SO_2) has an acceptable daily intake (ADI) of 0.7 mg kg^{-1} body weight [3].

The Monier-Williams (MW) method, which follows the AOAC official method 990.28-990.31 [4], is the most commonly used method for the determination of sulfite in food and drinks. This procedure is quite complicated and requires a lengthy distillation and titration process. The Ripper approach is also very popular in the spirit sector for analyzing sulfites. It is based on iodometric titration [5] which is comparably simple and unsophisticated, however, the red color of some drinks limit its application. Various methods for measuring sulfite in food and drinks have been developed, including chromatography [3, 6], flow-based approaches [7, 8], spectroscopy [9], and electroanalysis. These methods require the use of large and expensive instruments and the complex matrices in food and beverage samples is a concern that necessitates tedious sample preparation steps such as dissolution and extraction. For on-line analysis, flow injection with a gas diffusion unit is commonly used to analyze sulfites in food and spirit samples by converting sulfite into SO_2 by reaction with acid in a donor stream, followed by the analysis of SO_2 in an acceptor stream by amperometric detection [10], capacitively coupled contactless conductivity detector (C4D) [11], and spectrometric detection [12-15]. Spectrometric detection involves the reaction of SO_2 with specific colorimetric reagents such as malachite green and pararosaniline [14], p-aminobenzoate [12] , bromocresol green [13] and anthocyanin from roselle extract [15]. These colorimetric reagents provide satisfactory selectivity and reliable performance. However, some of them are carcinogens and some of them might be replaced by natural reagents, even though the natural reagents suffer from problems associated with the robustness of roselle extracts.

Flow analysis is one of the automatic methods that is commonly used in the food and beverage industries. However, it often requires the equipment to be connected individually [16], making the system large and requiring a skilled person to operate the system.

The objective of this work was to design and assemble an automatic analyzer for determining sulfite compounds in dried fruits and beverages. The system incorporates a gas diffusion unit (GDU) in which sulfite is converted into SO_2 gas and selectively used to reduce Fe(III) into Fe(II). This results in the formation of an Fe(II)-phenanthroline complex, which is then detected optically with the use of an integrated homemade optical sensor.

2. Materials and Methods

2.1 Reagents and chemicals

The chemicals used in this work were analytical reagent grades and used without further purification. Sodium sulfite (≥98%), ethylenediaminetetraacetic acid disodium salt dihydrate (99.0-101.0%), 1,10-phenanthroline monohydrate (99%), Fe(III) nitrate monohydrate (≥98%) and sodium hydroxide (≥97%) were purchased from

Sigma-Aldrich (St Saint Louis, MO, USA). Hydrochloric acid (HCl) (≥37%) and acetic acid (99.8%) were obtained from QReC, (Auckland, New Zealand). Deionized water used throughout the experiment was generated using ELGA LabWater Type II, Option 3 (High Wycombe, UK).

2.1.1 Standard solution

A stock standard of sulfite 1000 mg L^{-1} (as SO_2) was prepared by dissolving 0.1969 g of sodium sulfite in 100 mL of 1 mmol L^{-1} ethylenediaminetetraacetic acid aqueous solution (EDTA). The concentration of the sulfite stock standard solution was standardized by iodometric titration.

2.1.2 Colorimetric reagent

The 1,10-phenanthroline (Phen) solution (0.2 mol L^{-1}) was prepared in DI water, and a stock solution of 0.05 mol L^{-1} iron(III) nitrate was made in 0.3 mol L^{-1} hydrochloric acid. An acetate buffer (pH 5.5) was prepared by mixing 35 ml of 1 mol L^{-1} acetic acid and 15 mL of 2 mol L^{-1} sodium hydroxide solution. The colorimetric reagent was prepared by mixing 3 mL of iron(III) nitrate solution, 27.5 mL Phen solution, and 25 mL of acetate buffer solution, and the obtained mixture was then diluted to 250 mL with DI water. The reagent solution was prepared daily.

2.2 Design and assembly of the automated analyzer

The system components were assembled as shown in Fig. 1. It consists of two peristaltic pumps (Leadfluid BT50s, Shanghai China), making a two-line manifold for regents and samples delivery, a six-port injection valve (Idex V-24, Salt Lake USA) for fluidic control, and a home-made detection unit consisting of a flow-through cell and optical sensor. The system was controlled by a personal computer. A reaction coil and tubing for solution manipulation throughout the system was made of silicone tubing (ID 1 mm, OD 1.6 mm from VICI, Waterbury USA).

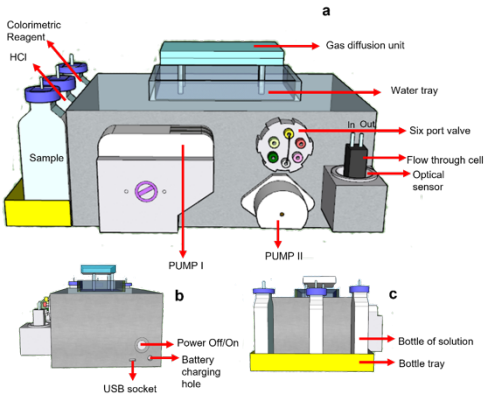

Fig. 1. Design of sulfite analyzer. The system consists of PUMP I for propelling the colorimetric solution (receiver) and HCl solution (donor); and PUMP II, for dispensing the standard/sample solution into a six-port valve; a gas diffusion unit; and the optical sensor (a). The right-hand side of the analyzer shows a position of a power off/on, battery charging hole, and USB socket (b); and the left side consists of a tray for placing bottles of reagent and sample solutions (c).

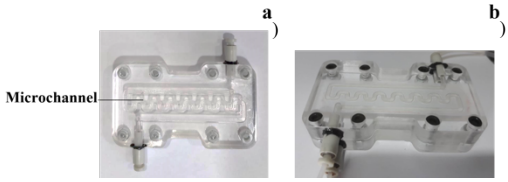

Fig. 2. Gas diffusion unit (GDU); (a) the microchannel and (b) two symmetric acrylic blocks.

2.2.1 Gas diffusion unit (GDU)

Two symmetric acrylic blocks (40 mm width × 70 mm length × 9.0 mm thickness) were used as a platform of GDU. The channel in this GDU was microfabricated using a CO_2 laser engraving machine (CNCBro, Shandong China) and its dimension was 2.5 mm width × 208 mm length × 0.8 mm depth, as shown in Fig. 2. The serpentine channel architecture design has been used to increase the surface area for gas diffusion and enhance the reaction product in the acceptor stream. The PTFE gas membrane, 19.0 mm width × 70.0 mm length × 0.1 mm thickness, (Towai,

Bangkok Thailand) was placed between two plates. PTFE tubing with 1.0 mm id. (VICI, Waterbury USA) was used for fluidic manipulation/connection throughout the system.

2.3 Apparatus and analytical procedure

The acceptor and donor stream supply the colorimetric reagent and HCl, respectively. In the first step, they were propelled at a flow rate of 0.4 mL/min for 1 min by PUMP I. In the second step, PUMP I was stopped, and the device set to zero absorbance for 5 seconds. In the third step, the sample/standard solution were propelled into the loop of the six-port valve using PUMP II. Next, PUMP II was stopped and a volume of 30 µL sample/standard solution in a loop was injected into the HCl stream at a flow rate of 0.4 mL/min for 40 seconds by PUMP I. Then, PUMP I was stopped for 5 min for extraction. In this step, sulfite reacted with HCl to generate SO_2 gas, which was then diffused through the PTFE membrane and the acceptor stream in GDU where it reduced Fe (III) to Fe (II) which then produced the red solution of Fe(II)-phenanthroline complex in an acceptor stream. The mixing coil (1.0 mm i.d. ×100 mm length) was used to improve the sensitivity of the reaction. Finally, the red solution was propelled into the flow-through cell at a 0.4 mL/min flow rate for 250 seconds using PUMP I and the color product was monitored with the optical sensor. The analytical signal was recorded as a peak height between the absorbance unit and time (second) (see Table 1). The manifold is schematically depicted in Fig. 3. The pumps, six-port valves, and the detection system were controlled using a computer with C programming language. Also, the software used to generate the calibration curve and compute the concentration of sulfite (as SO_2) in standards and samples.

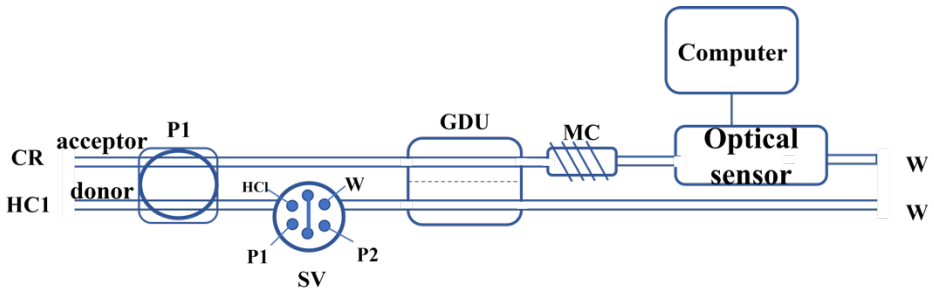

Fig. 3. A manifold of automatic sulfite analyzer on gas diffusion system via optical sensor CR: colorimetric reagent, HCl: hydrochloric, P1 and P2: peristaltic pump I and II, SV: six-port valve, GDU: gas diffusion unit, MC: mixing coil, and W: waste.

Table 1. Summary of operation steps of automatic sulfite analyzer.

Steps	Process	Flow rate (mL/min)	Time (s)	Operating
1	Run pump I	0.4	60	Washing
2	Stop pump I	-	5	Setting zero absorbance
3	Run pump II	2.0	5	Loading sample
4	Stop pump II Run pump I	- 0.4	- 40	Injecting sample
5	Stop pump I	-	300	Extraction time
6	Run pump I	0.4	250	Flux color solution
7	Stop pump I	-	-	Reading Absorbance and concentration

2.4 Sample preparation

All samples were purchased from a supermarket in Pathum Thani, Thailand. The spirit drinks and coconut juices were filtered prior to the analysis, whereas dried fruit samples were powdered and an accurate mass of 0.200 g was placed into a centrifuge tube, and extracted by adding 10 mL of distilled water. The mixture was centrifuged at 3000 rpm for 15 min, and then filtered using a syringe filter (Nylon membrane 0.45 μm, 25 mm diameter, Sartorius Lab Instruments, Germany). To minimize interference from metal ions, 5.0 mL of the filtrate sample was combined with 1 mL of 0.01 mol L^{-1} of EDTA solution, then diluted to 10 mL using DI water, and lastly the sulfite content in samples was determined with the developed automatic sulfite analyzer. For comparison, the samples were analyzed by the iodometric method [5].

2.5 Optimization

Univariate optimization was performed using 10 mg L^{-1} of sulfite (as SO_2) and for signal optimization the influence of the most influential parameters was investigated. These include: extraction time (0, 2 , 4, 6, 8, 10, 12, 14 and 16 min), concentration of HCl (0.05, 0.10, 0.50, 1.00, 1.50, 2.00, 2.50, 3.00, 3.50, and 4.00 mol L^{-1}), the reagents' concentration (0.1, 0.2, 0.4 0.6, 0.8, and 1.0 and 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24 and 26 mmol L^{-1} for iron(III) nitrate and Phen, respectively. The mixing coil length (0, 10, 15, 25, 50, and 100 cm) were also investigated. Initial conditions included 1.0 mol L^{-1} HCl, 2.0 mmol L^{-1} Phen, and 0.1 mmol L^{-1} iron(III) nitrate in the reagents' condition. Three replicate measurements were taken for each parameter.

2.6 Analytical features

The calibration curve was generated by graphing mAbs versus sulfite concentration in the range of 0.1-40.0 mg L^{-1} (N=3). The limits of detection (LOD) and quantitation (LOQ) were calculated by three and ten times the standard deviation of blank, respectively. The selectivity was examined by adding potential interfering species at 10–1000 mg L^{-1} to a sulfite solution of 10 mg L^{-1}. The added species were those commonly found in beverages, such as ascorbic acid, sodium nitrite, sodium sulfide, sodium bicarbonate, tartaric acid, boric acid, sucrose, fructose, and glucose. Furthermore, the influence of a 10% ethanol level on the sulfite signal was investigated. The evaluation was based on the signal's percentage difference from the control signal. Sulfite concentrations of 0.3, 1.0, and 10.0 mg L^{-1} (as SO_2) were spiked into samples to calculate the percentage recovery.

3. Results and Discussion

3.1 Effect of stopping time

As mentioned in the experimental section, the sulfite standard solution 10 mg L^{-1} reacts with hydrochloric acid in the donor stream in GDU to generate SO_2 gas which is then diffused through the membrane and dissolved in the receiver stream whereby it reduced Fe (III) to Fe(II). The reaction was studied by varying the time during which the pump propelling the standard into the donor stream was stopped for specific time interval (0-16 min). As shown in Fig. 4(a), the obtained absorbance signal is steadily increased as a function of pump stopping time until 4 min; thereafter, the signal is slightly increasing with time. Hence, the stopping time was set at 5 min to compromise between sensitivity and speed of analysis.

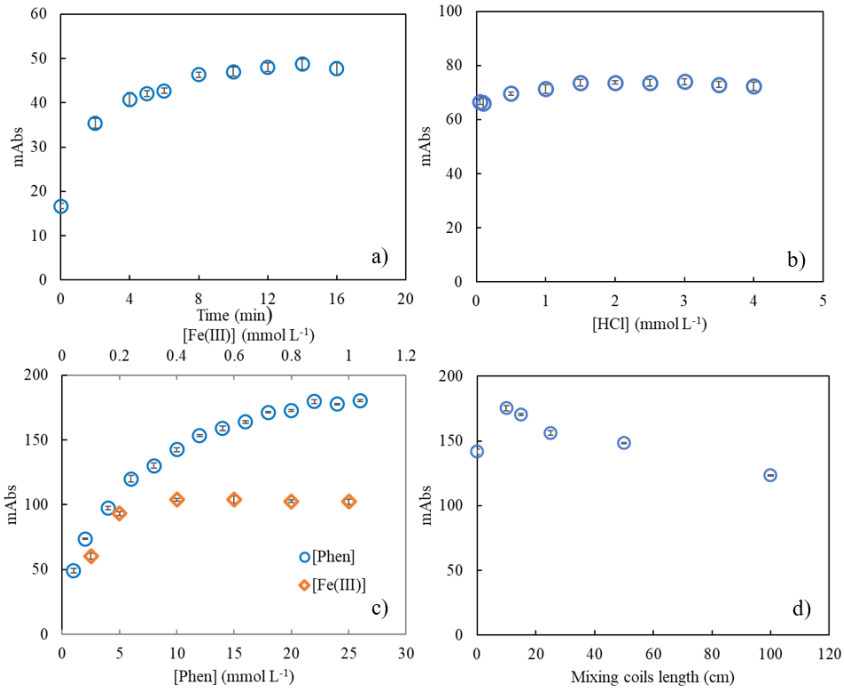

Fig. 4. Study effects of the most influencing parameters; stopping time (a), concentration of hydrochloric acid (b), concentration of Fe(III) and Phen (c), and mixing coil length (d).

3.2 Effect of hydrochloric acid concentration

HCl solution has a potential influence on the process because the conversion of sulfite ion SO_3^{2-} to SO_2 gas takes place at low pH to H_2SO_3 (pH < 3) according to the molecular distribution of sulfite species. Therefore, the concentration of HCl reacted with sulfite (0.05 - 4.00 mol L^{-1}) was studied. Evidently, increasing the concentrations of HCl beyond 1.5 mol L^{-1}, has minor influence on the absorbance signal of the red complex (Fig. 4(b)). Therefore, the acid concentration of 1.5 mol L^{-1} was chosen in this method.

3.3 Effect of colorimetric reagent concentration

As can be seen in Fig. 4(c), the absorbance signal rises steadily up to 0.4 mmol L^{-1} of Fe(III), and thereafter remains essentially constant. However, optimal condition selection requires contemplating both sensitivity and robustness. Therefore, the signal observed using 0.6 mmol L^{-1} of iron(III) nitrate has been chosen as the optimum. Similarly, the concentration of Phen was investigated over the range (1.0-26.0 mmol L^{-1}). Maximum absorbance intensity was achieved at a concentration of 22 mmol L^{-1} of the reagent, as indicated in Fig. 4(c), and afterwards remained almost constant.

3.4 Effect of mixing coil length

Investigation of the effects of varying coil lengths from 0 to 100 cm was conducted. It was expected that with a longer coil, the diffused SO_2 and colorimetric reagent were better mixed, resulting in a stronger absorbance signal (Fig. 4(d)). However, the use of long mixing coil resulted in a wider peak and lower peak height due to the increased dispersion. Also, the time spent on analysis is more likely to be prolonged. Therefore, the 10.0 cm length of mixing coil was chosen for this study since it yielded the signal with the greatest intensity.

3.5 Key analytical features

When operated at the optimized conditions, the response signal in mAbs unit was dependent on sulfite concentration over the range 1.0-35.0 mg L^{-1}. A non-linear calibration curve with equation;

$y = -0.1354x^2 + 14.766x + 21.755$ ($R^2 = 0.9991$) was acquired. The deviation from linearity is expected because the procedure does not only involve complex formation and reduction of Fe(III), but also a microextraction with gas diffusion unit which resulted in non-linear response at higher concentrations. The LOD and LOQ were calculated by 3 and 10 times the standard deviation of blank and were found to be 0.3 and 1.1 mg L^{-1} as SO_2, respectively. The 10-replicate analysis for sulfite standards at concentration of 1, 10, and 35 mg L^{-1} were demonstrated by percentage relative standard deviation (%RSD) of 4.5, 2.8, and 0.5, respectively.

The recovery data obtained by spiking standard sulfite at 0.3, 1.0, and 10.0 mg L^{-1} (as SO_2) into sample solutions and the results are presented in Table 2. The relatively high recovery values, 94.4-107.7% (N = 3), indicate that the proposed method is reliable for determining sulfite in the analyzed samples.

Table 2. Recovery study by spiking standard into the sample solutions.

Sample	Add (mg L^{-1})	Found (mg L^{-1})	Recovery (%
White wine	0.30	0.30 ± 0.001	99.0
	1.00	1.03 ± 0.004	103.0
	10.00	9.87 ± 0.002	98.7
Mix of raisins and cranberries	0.30	0.32 ± 0.001	107.7
	1.00	0.97 ± 0.001	97.3
	10.00	9.44 ± 0.004	94.4

3.6 Interference study

The effect of different interfering substances on the analytical signal of a 10 mg L^{-1} standard solution was investigated. Table 3 shows the results. The organic acids and carbonate (100 mg L^{-1}) and sugar (1000 mg L^{-1}) have no effect on the analyte signal (less than 5% error). However, a concentration of nitrite and sulfide ions of 10 mg L^{-1} influenced the sulfite signal (greater than 5%). Nitrite is often employed as an antibacterial and color enhancer, and bacteria in food can produce sulfide. The sulfide ion displayed a positive error due to a double displacement reaction between sodium sulfide and acid, which released H_2S gas, that could convert Fe(III) to Fe(II) as well as SO_2 [17], and nitrite, which can oxidize sulfite to sulfate. This led to a decline in SO_2 concentration and a negative error [18]. Fortunately, regular wines and dried fruits contain less than 10 mg L^{-1} nitrite and sulfide.

Table 3. Effects of potential interfering compounds on sulfite measurement.

Compound	Concentration (mg L^{-1})	% Error
Glucose	1000	-2.9
Fructose	1000	-1.1
Sucrose	1000	-3.2
Oxalic acid	100	-3.2
Ascorbic acid	100	-3.2
Tartaric acid	100	-0.7
Boric acid	100	-2.1
Carbonate	100	3.0
Bicarbonate	100	-2.6
Nitrite	10	-70.3
Sulfide	10	30.5
Ethanol	10*	-4.6

* % by volume

3.7 Analysis of samples

As mentioned in Section 2.4, the suggested analytical system was used to determine the sulfite levels in spirit drinks, coconut juice, and a mixture of raisins and cranberries, and the results were compared to an iodometric titration method (as shown in Table 4). The results of the developed approach agreed with those of the standard method. T-test tests at P 0.05 (t_{stat} 0.16 and t_{crit} 2.18, respectively) demonstrate no significant difference.

3.8 Comparison with some analytical methods

Literatures show that there are several flow-analysis systems coupled with gas diffusion units for the determination of sulfite

in various samples. Some examples of the reported work including the concentration range and LOD are listed in Table 5. The method developed in this work has a detection limit lower than those from C4D [11], photometric [14, 15], and pH detection method [21]. Our approach provides a wider concentration range, with the only exceptions being p-amino azobenzene as a colorimetric reagent [12]; and pH detection [21]. Although the proposed method provided a narrower range and higher LOD than amperometric determination [10], and spectrophotometric detection [14], it exhibited an advantage in terms of automation and convenience of use. In comparation to the study conducted by Danchana et al. [22], which employed an automated system with a multipumping module and a conductivity detector and presented a LOQ of 10.2 mg L^{-1}, this work proposed a lower LOQ of 1.1 mg L^{-1}. Therefore, this proposed method is suitable for the analysis of sulfite in food and drink industry.

Table 4. Comparison of the proposed and Ripper methods for sulfite determination in samples (N = 3).

Sample	SO_2 (mg L^{-1})	
	Proposed method	**Ripper method**
White wine 1	6.62±0.004	6.52±0.03
White wine 2	10.32±0.003	10.46±0.04
White wine 3	5.55±0.001	5.23±0.05
White wine 4	9.89±0.003	10.07±0.02
White wine 5	2.43±0.001	3.01±0.03
White wine 6	1.41±0.001	1.54±0.02
White wine 7	1.21±0.001	1.60±0.02
Sparkling wine 1	7.20±0.003	7.23±0.02
Sparkling wine 2	7.80±0.003	6.51±0.04
Rose wine 1	3.15±0.005	2.69±0.02
Rose wine 1	2.33±0.003	2.76±0.01
Coconut juice	5.51±0.003	5.25±0.04
Mix of raisins and cranberries	5.26±0.002	5.52±0.04

Table 5. Comparison of a flow-based system coupled with a gas diffusion unit for determination of sulfite.

Year	Sample	Detection method	Range (SO_2, mg L^{-1})	LOD (mg L^{-1})
1991 [12]	White wine, red wine and rose wine	Spectrometry with p-amino azobenzene as the colorimetric reagent	5-300	2.0
1997 [13]	White wine, red wine and rose wine	Spectrometric pH detection	0.8-16.0	0.08
2008 [10]	White wine and red wine	Amperometry	0.16-16.0	0.04
2009 [14]	White wine and red wine	Spectrometry with Malachite Green/ Pararosaniline)	25-250	0.8
2011[19]	Fruit juices	Supramolecular amperometric detector	0.51-5.1	0.03
2013 [20]	Wine and molasses	Spectrometry with Malachite Green	2.0-16.0	0.2
2017 [21]	Wines	pH detection	1-60	0.5
2019 [22]	Wines	Multi-pumping module and Conductivity	10.2-76.2	-
2020 [11]	White wine and red wine	C4D	4.0-20.0	1.92
2021 [15]	Sparkling wine, white wine, red wine	Spectrometry with Roselle natural reagent	4.0-80.0	1.6
This work	Wines, juices and dried fruit	Spectrometry with Fe(III)+o-Phenanthroline	1.0-35.0	0.32

4. Conclusions

An automatic sulfite analyzer has been assembled by the integration of microfabricated microflow gas diffusion and miniaturized optical sensor as adaptable tools for the colorimetric detection of sulfite in beverages and dried fruits. The utilization of a microflow gas diffusion unit in the technique is a potential solution for mitigating interference in sample solutions. Nevertheless, the presence of nitrite and sulfide ions at a concentration of 10 mg L^{-1} had an impact on the analysis of sulfite. Fortunately, the concentration of these ions in normal wines and dried fruits is lower than the specified threshold. The method exhibits a well-calibrated graph

with a suitable limit of detection (LOD). The procedure enabled the quantification of sulfite in real samples, exhibiting a level of precision that is equivalent to the established Ripper method. The novelty of the suggested analytical device is characterized by its automation, portability, user-friendly operation, and potential to supplant complex equipment that necessitates skilled operators.

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