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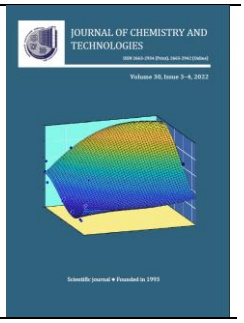

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IN-VESSEL HEADSPACE LIQUID-PHASE MICROEXTRACTION HYPHENATED WITH SPECTROPHOTOMETRIC DETERMINATION OF SULFITE WITH ELLMANN`S REAGENT

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Abstract

A new, simple, highly sensitive and selective method for the spectrophotometric determination of sulfite based on the preconcentration with in-vessel headspace liquid-phase microextraction method has been developed. It includes the release of sulfur dioxide vapor from 10 mL of an aqueous solution of sample in the reaction of sulfite with an excess of orthophosphoric acid and absorption by 100 µL of 0.1 mM 5,5`-dithiobis-(2-nitrobenzoic) acid. The acceptor phase was placed in the headspace above the solution in a specially designed container. The extraction takes 20 min by stirring of the sample solution with 1200 rpm. The absorbance was measured at 350 nm in a quartz microcuvette with a volume of 50 µL and an optical path of 10 mm. The calibration graph is linear in the range from 26 to 260 µg L^{-1} (as SO_2) with a detection limit of 8 µg L^{-1}. The developed method was successfully applied to determine the content of sulfite in alcoholic drinks, jam, and juices.

Keywords: In-vessel headspace liquid phase microextraction; sulfite determination; spectrophotometry; analysis of juice, jam and alcoholic drinks.

ПАРОФАЗНА МІКРОЕКСТРАКЦІЯ У РЕАКТОР СПОЛУЧЕНА З СПЕКТРОФОТОМЕТРИЧНИМ ВИЗНАЧЕННЯМ СУЛЬФІТУ З РЕАКТИВОМ ЕЛЬМАНА

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Анотація

Розроблено новий, простий, високочутливий і селективний метод спектрофотометричного визначення сульфіту, який грунтується на попередньому концентруванні методом парофазної мікроекстракції у реактор. Він включає виділення діоксиду сірки з 10 мл водного розчину зразка в реакції сульфіту з надлишком ортофосфорної кислоти та поглинання 100 мкл 0.1 мМ 5,5`-дитіобіс-(2-нітробензойної) кислоти. Акцепторну фазу поміщали у газовій фазі у спеціально розробленому контейнері над розчином. Екстракція триває 20 хв при перемішуванні розчину зразка зі швидкістю 1200 об/хв. Оптичну густину вимірювали при 350 нм у кварцовій мікрокюветі об'ємом 50 мкл і товщиною поглинаючого шару 10 мм. Градуювальний графік є лінійним у діапазоні від 26 до 260 мкг L^{-1} (як SO_2) з межею виявлення 8 мкг L^{-1}. Розроблений метод успішно застосований для визначення вмісту сульфіту в алкогольних напоях, варенні та соках.

Ключові слова: парофазна мікроекстракція у реактор; визначення сульфіту; спектрофотометрія; аналіз соків, варення та алкогольних напоїв

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Introduction

Sulfur dioxide (additive E220) is widely used in the food industry as a preservative. This compound prevents the development of bacteria and fungi, inhibits the enzymatic darkening of vegetables and fruits, and slows down the formation of melanoidins. Another area of use for sulfuric anhydride is winemaking, thanks to its antibacterial, antioxidant and binding properties. But at the same time, this compound has a negative impact on human health [1]. According to wine industry specifications, a large amount of sulfite (up to 400 mg L^{-1}) is added to wine. All food products containing a sulfite concentration of more than 10 mg L^{-1} must be labeled accordingly [2]. In other food products, sulfites are used as inhibitors of enzymatic and non-enzymatic reactions during food preparation and storage. Sulfite ions also serve as an indicator of disruption of the sulfur conversion cycle in natural waters [3]. Despite all the advantages of use of sulfite ions in the food industry, their presence in large quantities can lead to asthma and allergic reactions in people with increased sensitivity, hypotension and food intolerance [4]. Asthmatics should be especially careful when using products treated with E220. Sulfur dioxide destroys vitamin B1, and completely destroys vitamin B12 in the body. In the European Union, the maximum permissible concentration of SO_2 for different types of wines is established from 160 mg L^{-1} for dry red wines to 300 mg L^{-1} for sweet white wines and 400 mg L^{-1} for botrytized wines. Therefore, the control of sulfur dioxide in food products and wines is an important parameter in the analysis of any food products. In the case of background pollution with sulfur dioxide and suspended particles, a concentration of 0.1 mg m^3 should be considered critical. The maximum one-time maximum permissible concentration of sulfur dioxide in the atmosphere is 0.5 mg m^{-3}, the average daily limit is 0.05 mg m^{-3}.

The food and beverage industry still needs a simple, inexpensive, and reliable method with sufficient selectivity and sensitivity to monitor low concentrations of free and bound sulfites in complex foods and beverages. In many cases, the determination of sulfite is carried out using spectrophotometry. This method is well combined with microextraction [5] such as micellar extraction with ultrasonic dispersion (UA-CPE) [6] and dispersive liquid-liquid microextraction (DLLME) [7]. The headspace liquid-phase microextraction (HS-LPME) is usually the most convenient choice for such approaches [8; 9].

Inexpensive and easy-to-use accessories for performing spectrophotometric measurements in relatively small volumes are now available, such as 50–100 μL microcuvettes and 5–10 μL ultramicrocuvettes. However, the combination of HS-LPME and UV-Visible spectrophotometry remains challenging, primarily because the commonly used acceptor phase volumes are very small (typically 1–3 μL). Recently, we have proposed a new headspace ME technique called in-vessel headspace liquid phase microextraction (IV-HS-LPME) [8; 10]. The principal feature of this approach is that the acceptor phase is held in a self-made reactor fixed in a headspace above the analyzed solution in a closed vial. The proposed approach is fully compatible with conventional microcuvettes and instruments used in spectrophotometry. The capabilities of the method were evaluated by determining iodide by its conversion to volatile I_2, the subsequent absorbtion of the latter by 1% KI and, finally, by measuring the absorbance of the I_3^- complex in a microcuvette [8]. The developed method was also successfully used to determine a number of other inorganic compounds in various objects of analysis [10–12]. This approach has been successfully used to fix the extraction phase in the hole of an optical probe [11; 12].

The purpose of this study is to develop a simple, relatively fast, selective and sensitive spectrophotometric method for the determination of sulfite in beverages and foods containing sulfur dioxide as a preservative, and to further validate the recently proposed IV-HS-LPME approach for preconcentration and separation.

Experimental part

Reagents and equipment. All chemicals used were of analytical grade purity. Double-distilled water was used throughout the study.

A 0.01 mol L^{-1} Na_2SO_3 stock solution was prepared by dissolving the salt in distilled water and was stored for no more than two weeks. This solution contained 2.5 mL of 0.01 mol L^{-1} EDTA to eliminate the possible interference effects of metal cations. The working solution of sulfite was prepared each day. Ortho-phosphoric acid was used to acidify the sample solution. Solutions of other acids were prepared by diluting the appropriate amount of acid with distilled water. To prepare the 1 mmol L^{-1} stock solution of 5,5`-dithiobis-(2-nitrobenzoic) acid (DTNB), 19.8 mg of DTNB was dissolved in 5 mL of ethanol and

diluted with a 0.1 mol L^{-1} pH 7.0 phosphate buffer up to 50 mL in a volumetric flask. 0.01 mol L^{-1} and 1 mol L^{-1} solutions of interfering substances were prepared by dissolving appropriate amounts of them in distilled water. The phosphate buffer with pH 7 was prepared by dissolving 9.343 g K_2HPO_4 and 6.309 g KH_2PO_4 in distilled water and diluting it up to 1000 mL.

Absorbance and absorption spectra were measured on an SF-46 spectrophotometer (LOMO, St. Petersburg, Russia) equipped with glass cuvettes with an optical path length of 10 mm. Micro-volume quartz cuvette (Starna Scientific Ltd., UK) with a path length of 10 mm (50 μL) was used to measure the absorbance. A magnetic stirrer (RIVA-03.2, UOSlab, Ukraine) with heating and electronic speed control was used to mix the solutions. Experiments were performed in a 15 mL pharmacy vial equipped with a rubber stopper (Fig. 1). A plastic or glass vessel designed to hold the acceptor phase was secured with a wire in a rubber stopper. The pH was monitored on a pH-150 MI pH meter with an ES-10601 glass indicator electrode and an ESD-10101 silver chloride reference electrode.

a **b**

Fig. 1. Experimental setup for the determination of sulfite by IV-HS-LPME method (a) and rubber stopper with attached plastic vessel containing acceptor phase and equipped with an insulin syringe to deliver H_3PO_4

Procedure for sulfite determination. 10 mL of a sample solution containing sulfite in the concentration range from 30 to 300 μg L^{-1} was placed in a 100 mL flat-bottomed flask. The flask was closed with a rubber stopper, into which a vessel with an acceptor phase and a syringe for acid injection were fixed. The acceptor phase was 100 μL of a 0.1 mM DTNB solution in a phosphate buffer solution with pH 7.0. To initiate the reaction of sulfur dioxide evolution, 0.8 mL of 10 M phosphoric acid was added to the sample solution. The solution was stirred on a magnetic stirrer at 1000 rpm for 20 min. After that, the extraction phase was transferred with a microsyringe into a microcuvette with a volume of 50 μL and the absorbance was measured at 412 nm.

Analysis of juices. The matrix effect was eliminated by diluting the juice to 10 mL. 0.5 mL of juice was added to the vial and diluted to approximately 10 mL with distilled water. When adding a larger portion of juice due to the presence of a large amount of citric acid, the analytical signal increases significantly and disproportionately. In this case, known amount of analyte was added to the another vial, and the sulfite content was determined by a standard addition method using a previously constructed calibration graph and the procedure described above.

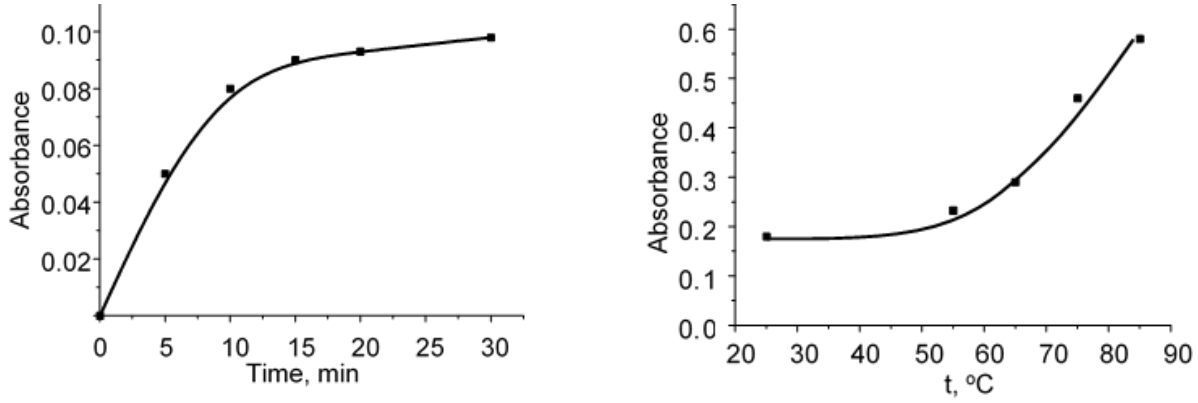
Analysis of jam. 4.1 g of jam was dissolved in 50 mL of distilled water, and the solution was filtered. 0.1 mL of the obtained solution was introduced into the vial, diluted with water to 10 mL and the sulfite content was determined by the standard addition method using a previously constructed calibration graph and the procedures described above.

Analysis of beverages containing alcohol. Content of free sulfur dioxide was determined in wines. Taking into account the high content of sulfite, 0.1 mL of wine or cider was sufficient for the analysis of alcoholic beverages. Tartaric acid can interfere with wine analysis. The matrix effect was eliminated by diluting the samples. After that, the analysis was continued as described above.

Results and discussion

Chemistry of the method and choice of a reagent for sulfite determination. In this work, for the determination of sulfite, a method is proposed, which involves the conversion of sulfite into volatile sulfur dioxide by reaction with an acid and its subsequent absorption by a reagent solution with the formation of a colored product. The sample solution is placed in a hermetically sealed vial, and the reagent solution is placed above the sample solution in a vessel, which is fixed in a rubber stopper. Two substances were studied as a reagent, including the iron(III) phenanthroline complex and Ellman`s reagent.

The study of the reaction between the iron(III) phenanthroline complex and sulfur dioxide released from sulfite was carried out according to the following procedure. 10 mL of a solution containing a certain amount of sodium sulfite was added to a 100 mL flat-bottomed flask and heated in a thermostat to 85 °C. 0.12 mL of 1 mM $FeCl_3$, 0.06 mL of 0.5% phenanthroline, 0.06 mL of acetate buffer solution with a pH of 5.5 were placed in a 2 mL reagent vessel, which was secured with a rubber stopper. The reagent solution in vessel was brought to 0.5 ml with distilled water and stirred. An excess of 1 M hydrochloric acid was added to the flask, quickly closed with a stopper with a reagent container attached to it, and kept in a thermostat at a temperature of about 85 °C for 15 min. After the end of the headspace extraction, the solution from the container with the reagent was transferred to a 1 cm cuvette, and the absorbance was measured at 510 nm.



a **b**

Fig. 2. Dependence of absorbance of the acceptor phase on extraction time (a) and temperature of the donor phase (b) in the determination of sulfite by IV-HS-LPME method. m(Na_2SO_3) = 0.16 mg, C($FeCl_3$) = 0.08 mM, C(o-phenanthroline) = 0.02 %, pH = 5.5, V (donor phase) = 10 mL, V(acceptor phase) = 0.5 mL, λ = 510 nm, l = 1 mm.

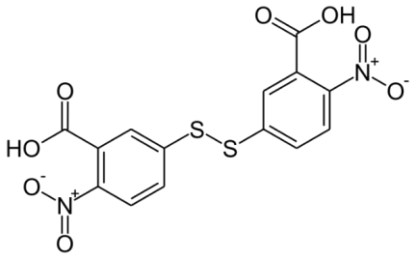
It was confirmed that the reaction between sulfite and iron(III) phenanthroline proceeds slowly and takes at least 5 min at room temperature (Fig. 2a). In the studied case, the total analysis time is more dependent on the duration of the extraction stage. Absorbance of the extraction phase rapidly increases up to 10 min, after which a further increase in absorbance slows down (Fig. 2a). For further experiments, an extraction time of 15 min was chosen. The temperature of the sample solution greatly influences the rate and completeness of the formation of the colored product of the iron(II) complex with o-phenanthroline in the acceptor phase (Fig. 2b). The analytical signal rises slowly up to 65 °C, after which it rises more rapidly. Therefore, the temperature of the sample solution should be maintained as much as possible. 85 °C was chosen as optimal, since at a higher temperature the possibility of leakage increases significantly.

Thus, the studied approach to the sulfite determination makes it possible to obtain a high concentration of the intensively colored iron(II) complex in the acceptor phase. However, the reaction is poorly reproducible, mainly because it requires prolonged heating at a high temperature. Therefore, we tried to find a more suitable extraction reagent.

DTNB is commonly used as an efficient reagent for the determination of thiols in biochemical samples. The use of DTNB was extended to the reaction with sulfite ions (SO_3^{2-}) [13; 14]. Sulfite replaces the thiol anion to form an organic thiosulfate, called «Bunte» salt

$$RSSR + SO_3^{2-} = RSSO_3^- + RS^- \quad (1)$$

where R is



Optimization study. Influence of acidity of sample solution. A lot of parameters influence the IV-HS-LPME determination of sulfite with Ellmann`s reagent including those related with the composition of donor and acceptor phases. Nature and quantity of acid added to the donor phase are most important parameters determining the analytical signal in the proposed method. Hydrochloric, nitric, sulfuric and orthophosphoric acids were tested. Preliminary experiments have shown that for all studied acids after certain time on the dependence of absorbance of acceptor phase on the extraction time significant decrease of the analytical signal is observed (Table 1). Especially strong is absorbance dropping in the case of hydrochloric and nitric acids. It is obvious that volatility of these acids is the reason for such undesired reactions.

Table 1

The effect of different acids on the absorbance of the extraction phase in the spectrophotometric determination of sulfite with preconcentration by IV-HS-LPME method. C(Na_2SO_3) = 3.5 μM, C(DTNB) = 0.1 mM, pH 7, stirring rate 1000 rpm, extraction time 10 min, λ = 412 nm, l = 1 cm

Acid	Time of extraction, min	A
1.2 M HCl	15	0.550
	30	0.070
1.2 M HNO_3	15	0.101
	30	0.057
1.0 M H_3PO_4	15	0.563
	20	0.620
	30	0.580
0.6 M H_2SO_4	15	0.790
	30	0.660

The vapors of acids trapping in the acceptor phase shift the pH of the solution to the values for which the reagent and «Bunte» salt can be destructed. It is well known [11; 13] that sulfite completely reacts with DTNB only at pH > 6. In addition, intensive stirring the solution leads to the formation of small drops of donor phase which can also trap into the acceptor phase and acidify it. Thus, it is recommended to prepare the buffer solution with high buffer capacity. Influence of less volatile sulfuric and particularly phosphoric acid is noticeably less. Moreover, for the phosphoric acid at the high buffer concentration dependence on time takes the form of common kinetic curve [11]. Taking this into account, orthophosphoric acid was chosen to acidify the sample solution. Investigation of the influence of orthophosphoric acid concentration on the absorbance of the extraction phase has shown that growth of the absorbance continues up to 0.8 M after that the curve levelled out. This concentration was taken as optimal in subsequent experiments.

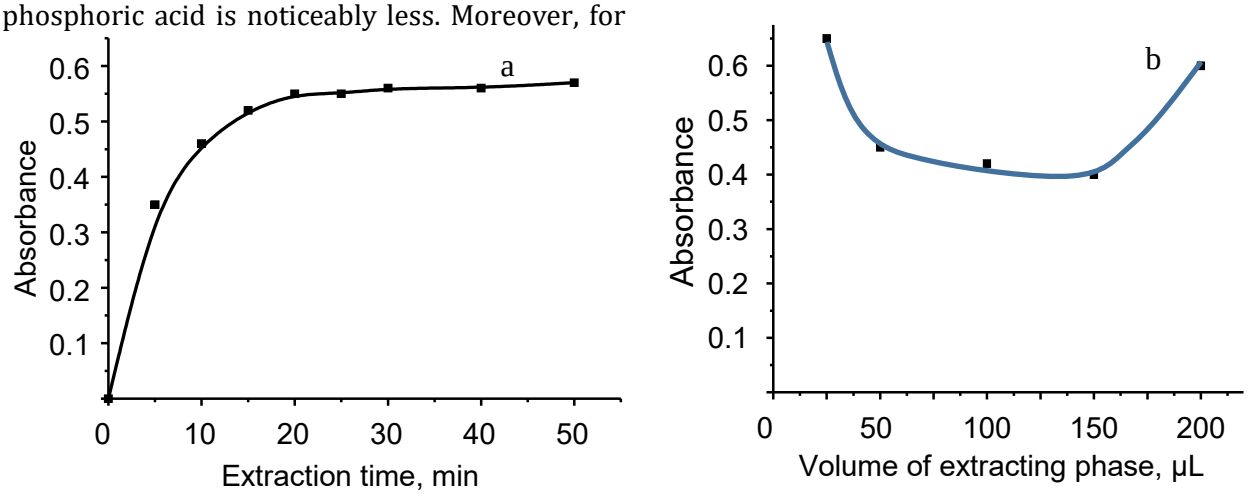


Fig. 3. Influence of extraction time (a) and volume of extraction phase (b) on the absorbance of extraction phase. C(Na_2SO_3) = 3.5 μM, C(DTNB) = 0.1 mM, C(H_3PO_4) = 0.83 M, pH 7, stirring rate 1000 rpm, extraction time 10 min, volume of sample solution = 10 mL, volume of extraction phase = 100 μL, 412 nm, l = 1 cm

Influence of extraction time, temperature and stirring rate of the donor phase. The reaction between DTNB and sulfite in the solution is complete after about 8 min. The overall duration of the determination depends mainly on the stages of headspace extraction, mass transfer in the acceptor phase, and the slow reaction between analyte and reagent in the acceptor phase. As can be seen from Fig. 3a, under optimal conditions, the absorbance reaches its maximal equilibrium value starting from 20 min of headspace extraction. A study of the effect of stirring speed showed that extraction equilibrium is reached when the magnetic stirrer speed is set to 1000 rpm. These parameters were taken as optimal. The influence of the temperature of the sample solution was investigated in the range from 20 to 55 °C. The absorbance was constant between 20 and 30 °C, but at temperatures above 30 °C the signal was significantly reduced. It is likely that the reagent and reaction products with sulfite are unstable at elevated temperature. Therefore, there is no need to heat the donor solution, which simplifies the procedure.

Effect of pH and DTNB concentration in the acceptor phase. According to the literature [13], the most complete reaction of DTNB with sulfite occurs in the pH range from 6 to 9. To study effect of pH, a phosphate buffer was used in the pH range from 5.5 to 10. It was shown that absorbance was almost constant at a pH above 6. Phosphate buffer having pH 7.0 was used for further studies.

The effect of DTNB concentration in the acceptor phase on the extraction of sulfur dioxide from sodium sulfite solution was studied in the concentration range from 0.05 mM to 0.5 mM. It turned out that a concentration of 0.1 mM of the reagent is sufficient for the complete formation of the complex. After that, the absorbance of the solution almost does not change. For further experiments, a concentration of 0.1 mM DTNB was chosen.

Effect of volumes of acceptor and donor phases. A very important parameter for preconcentration is the enrichment factor [15]. At a constant volume of the acceptor phase, the enrichment factor can be increased by increasing the volume of the donor phase. The effect of the volume of the sample solution on the absorbance of the acceptor phase was studied in the range from 5.0 to 20.0 mL. With an increase in the volume of the donor phase, the analytical signal increases, but to a lesser extent than is determined by the increase in the ratio of the volumes of the donor and acceptor phases. This can be explained by insufficiently high partition coefficients between the donor and headspace phases, on the one hand, and the headspace and acceptor phases, on the other. When using 20 mL of donor phase, it takes more than 30 min to reach equilibrium. Therefore, 10 mL of donor phase was used to reduce the analysis time. If necessary, the sensitivity can be increased by increasing the volume of the donor phase, but at the expense of a significant increase in the duration of the analysis.

The enrichment factor can be increased not only by increasing the volume of the donor phase, but also by reducing the volume of the acceptor phase. The effect of this factor was studied in the range from 25 to 200 μL (Fig. 3b). The highest absorbance corresponds to the use of 25 μL of the acceptor phase. Absorbance is lower for the volumes greater than 50 μL but further decrease in the absorbance is not significant. At the same time, the absorbance of the blank experiment increases significantly from 100 to 25 μL. Since at 100 μL the blank absorbance is practically zero, this leads to a better reproducibility of the procedure. In addition, the volume of the microcuvette used in the work was 50 μL. Therefore, 50 μL of DTNB solution was used as the optimal volume of the extraction phase.

Calibration graph. The calibration graph for sulfite determination, built under optimal conditions, was linear in the range from 0.4 to 4 μM SO_3^{2-} (26-260 μg L^{-1} in units of SO_2 concentration) and the detection limit was 0.12 μM (8 μg L^{-1}). Equation of calibration graph was Abs = 0.012 + 208000×C(sulfite) with a correlation coefficient of 0.9957. Precision, measured in units of relative standard deviation, was 0.8 %. The enrichment factor was equal to 14, which corresponds to the extraction percentage of 14 %.

Interference. Since there is no contact between the donor and acceptor phases, the study of interference can be limited to volatile substances that can react with DTNB and components that can affect the release of sulfur dioxide from the donor phase. Nitrite is often used as an antimicrobial agent and color enhancer [16]. Some bacteria found in food and wine can release small amounts of sulfide [17]. The concentrations at which various substances do not interfere with the determination of sulfite are presented in Table 2.

Table 2

Effect of interfering substances on the determination of sulfite

Substance	Concentration, which does not interfere with the determination of sulfite, M
KI	10^{-5}
KNO_3	10^{-2}
KBr	5×10^{-3}
KCl	10^{-3}
NaF	10^{-3}
Na_2CO_3	10^{-3}
$NaNO_2$	10^{-7}
Oxalic acid	10^{-3}
Citric acid	5×10^{-4}
Ascorbic acid	10^{-3}
Tartaric acid	10^{-3}
Na_2S	10^{-6}
Na_2SO_4	0.1
$Na_2S_2O_3$	10^{-7}

Analysis of real objects. The developed IV-HS-LPME method was tested in determining the amount of sulfite in juices, jams and wines (Table 3). The matrix of juices, jams and wines can affect the process of sulfur dioxide release from the donor phase, so it is recommended to use the method of standard additions.

The determination of the actual content of sulfur dioxide in alcoholic beverages was carried out according to DSTU 4112.25-2002 [18]. The analysis of real objects for sulfur dioxide content was carried out by the iodometric method. The presence of a large amount of tartaric and other hydroxy acids in all samples of wine, as well as citric acid in apple-grape nectar and cider, leads to an overestimation of the sulfite content. The matrix effect can be removed by diluting the sample. For the analysis of samples containing a large amount of hydroxy acids, the method of standard additions was used. As can be seen from the Table 3, there are no significant differences between the added and found sulfite contents in the samples, which indicates the accuracy of the method used. For two samples, including white wine and champagne, the accuracy of the method was also evaluated by comparison with the results obtained by the standard iodometric method.

Table 3

Results of determination of sulfite in real objects by the IV-HS-LPME method

Object of the analysis	Found,[a] μM	Added, μM	Found by the proposed method, μM	
			Using the calibration graph	By standard addition method[b]
Cider "Somersby", Mango-Lime flavor	Not found	0	Not found	Not found
	–	0.96	–	1.03±0.14
	–	1.98	–	2.20±0.28
Apple-grape nectar "Sadochok"	Not found	0	Not found	Not found
	–	0.84	–	0.89±0.05
	–	0.5	–	0.47±0.03
Jam fruit and berry "blueberry" pasteurized Emmy	Not found	0	Not found	Not found
	–	1.02	1.11	–
	–	1.65	1.59	–
Kagor «Shabo»	Not found	0	Not found	Not found
		0.28	–	0.27±0.02
White wine "Muscat Vechirnya Odesa", Smart choice[c]	27.1	0	–	29.8±2.5
Champagne «Secco rosato, Frizzante, 2019»	756	0	–	732±34

[a] found by DSTU method [18]

[b] $x_{aver}\pm\Delta$, n = 5, 95% confidence level

[c] diluted one hundred times before analysis

Comparison of the proposed method with other methods. Comparative characteristics of the developed IV-HS-LPME method for the determination of sulfite ions with the other methods using microextraction preconcentration proposed in the literature are given in Table 4. UV-Vis spectrophotometric methods that do not use the preconcentration step have a significantly lower sensitivity than the proposed method [24]. The proposed method uses a rather large volume of the extraction phase (100 mL), which reduces the sensitivity of the developed method. By using a smaller volume of extractant, the detection limit can be reduced.

In a similar method using an optical probe, 25 μL of extractant was used [19]. At the same time, the detection limit for the proposed method is the same, and the enrichment factor is comparable to that obtained by Zaruba et al. An even greater difference between the enrichment factor and the achieved sensitivity is observed in the HS-SDME method proposed by Gómez-Otero et al [9]. An 80-fold decrease in the volume of the extraction phase led to an increase in sensitivity only by a factor of 3.5. This is because the extraction percentage was about 8 percent under the optimal conditions used in this method. In addition, the method of Gómez-Otero et al. has limitations in terms of extracting phase volume, microdrop displacement and solvent volatility. The small optical path used in the microvolume spectrophotometer contributes to reduced sensitivity. The disadvantage of this approach is also the use of less available and more expensive equipment.

The sensitivity of sulfite determination is much higher for CPE and DLLME microextraction methods [6; 7; 20–22]. However, they suffer from the influence of a dirty or complex matrix and the presence of solid particles in the sample. The developed method has a high selectivity and better reproducibility compared to microextraction methods previously described in the literature. In addition, unlike this group of methods, the IV-HS-LPME method does not require the use of organic solvents or surfactants and fully complies with the requirements of green analytical chemistry. The proposed method has comparable analytical performance to the HS-LPME-OP method [11], but uses more readily available equipment for the measurement of the absorbance.

Conclusions

The IV-HS-LPME method tested in this work demonstrates high selectivity and better reproducibility than other proposed methods for the determination of sulfite ions. The sensitivity of headspace microextraction for the determination of sulfite is less than of microextraction methods using direct contact between the sample and the extracting phases, but is within the same limits as previously proposed headspace microextraction methods. The determination method avoids the use of organic solvents harmful to the environment, which is in line with the principles of green chemistry. The determination process is quite fast and does not require significant sample preparation, which allows rapid analysis of samples. The use of headspace microextraction technique avoids the influence of many matrix components of complex samples. The proposed method has been successfully applied to the analysis of beverages, jams and alcoholic beverages.

Table 4

Comparison of microextraction methods for sulfite determination

Microextraction procedure	Method of detection	Reagent	Samples	LOD,[a] μg L^{-1}	Linear range,[a] μg L^{-1}	RSD (%)	References
HS-SDME	UV-Vis, OP	Fe (III), 1,10-phenanthroline	Wine, jams, juices	8	32–320	-	[19]
UA-CPE	UV-Vis	Nile blue A, Triton X–114	Drinks	1.75	6–180	2.4–5.2	[6]
DLLME	UV-Vis	o-Phthaldialdehyde	Drinking water, products	0.2	2–100	2.8	[7]
HS-SDME	UV-Vis	5,5`-dithiobis-(2-nitrobenzoic) acid	Fruits, vegetables, canned foods and wine	4	4–100	5.13	[9]
DLLME	UV-Vis	Fe (III), 1,10-phenanthroline	River and normal water	0.096	1.2–120	1.6–2.2	[20]
UA-CPE	FAAS	Fe (III), 5,6-diphenyl-3- (2-pyridyl) -1,2,4 triazine	Food and drinks	0.012	0.04–70	1.3–4.1	[21]
UA-CPE	UV-Vis	Toluidine blue, Triton X-45	Dried	1.15	2.5–350	2.1–	[22]

Continuation of table 4

			vegetables and fruits			4.8	
HS-TFME	SERS	-	Traditional chinese medicines	6	25–400	-	[23]
-	UV-Vis	Pentacyanidonitrosylferrate(II)	Wine, natural samples	990	1000–10000	-	[24]
HS-LPME-OP	UV-Vis, OP	DTNB	Alcoholic drinks, jams, juices	12	26–260	0.8	[11]
IV-HS-LPME	UV-Vis	DTNB	Alcoholic drinks, jams, juices	8	26–260	1.2	This work

[a] LOD and linear range are given in units of sulfur dioxide concentration
HS-SDME – Headspace single-drop microextraction; DLLME – Dispersive liquid–liquid microextraction; UA-CPE – Ultrasonic-assisted cloud point extraction; GDME – Gas-diffusion microextraction; SPCE – Screen-printed carbon electrodes; HS-TFME – Headspace thin-film microextraction; SERS – Surface enhanced Raman spectrometry.

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