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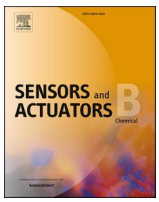

Capillary microfluidic platform for sulfite determination in wines

Manuel J. Arroyo [a], Ignacio de Orbe-Payá [a,c,*], Mariano Ortega-Muñoz [b,c], Jose Vilar-Tenorio [a], David Gallego [a], Gerhard J. Mohr [d], Luis Fermín Capitán-Vallvey [a,c], Miguel M. Erenas [a,c,*]

[a] ECsens, Department of Analytical Chemistry, Campus Fuentenueva, Faculty of Sciences, University of Granada, 18071 Granada, Spain
[b] Department of Organic Chemistry, Campus Fuentenueva, Faculty of Sciences, University of Granada, 18071 Granada, Spain
[c] Unit of Excellence in Chemistry applied to Biomedicine and the Environment of the University of Granada, Spain
[d] Institute for Surface Technologies and Photonics, Joanneum Research Forschungsgesellschaft mbH, Weiz, Austria

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ABSTRACT

A microfluidic paper-based analytical device integrating a chromoreactand – a formylazo dye– has been fabricated and used for a colorimetric assay of sulfites. The chromoreactand was covalently linked to paper by vinyl sulfone chemistry. This work presents two robust capillary microfluidic devices to determine sulfite in wine without any pretreatment. One of them based on thread (μTPAD) useful to determine it in white wine and another based on paper (μPAD) to specifically determine sulfite in red wine as well as in white wine. Both are based on the selective recognition of sulfite by means of a chromoreactand that turns from orange to yellow in the presence of sulfite.

The colour information acquired (H coordinate) using a digital camera readout allows for a range of application of the μTPAD from $7.8{\cdot}10^{-5}$ M (8.1 mg L^{-1}) to $2.7{\cdot}10^{-3}$ M (279.3 mg L^{-1}) with a limit of detection (LOD) of 78 μM.

The strong interference caused by the dyes present in red wine is eliminated by including a laminated paper channel in the μPAD structure that allows for the separation of colorants from red wine before the recognition of the sulfite. This makes it possible to adjust the μPAD procedure to the usual sulfite concentration in wine, with an LOD of $2.2{\cdot}10^{-4}$ M (22.7 mg L^{-1}) and a CV of 2.6%.

1. Introduction

Sulfite is a wine preservative that has been widely used since ancient Rome times due to its extreme chemical reactivity. It has antioxidant properties, inhibits enzymes and the Maillard reaction, is a reducing agent and has antimicrobial properties. Sulfite is generally added as calcium, sodium or potassium sulfites or hydrogen sulfites and belongs to the group of preservatives (E220–E228). Furthermore, in the United States, sulfite is designated as a GRAS (Generally Regarded as Safe) preservative [1]. At the end of the 1990s, its use began to be restricted due to the adverse reaction that occurs in people who suffer from asthma or are allergic to this type of compound. Currently, presence in a product must be indicated on the label if the sulfite concentration is higher than the legally established limit.

Sulfites are a natural preservative in some products, such as wines or beers [2], where they are produced during the fermentation process. In the case of wine, the European Union has established that it is mandatory to indicate the presence of sulfite if its concentration is greater than 10 mg L^{-1}, and a maximum concentration range of 150–500 mg L^{-1} has been defined, depending on the type of wine as well as its sugar concentration [3]. Therefore, sulfite determination is required for beverages, and a variety of different methodologies are available that must be performed in the laboratory, like redox titrimetry, chromatography, capillary electrophoresis, spectrophotometry, fluorimetry, voltammetry and amperometry [4]. Some of these have been implemented in different flow systems [5].

There is a significant demand for the development of point-of-need (PON) devices that can perform the analysis in-situ, by non-specialized personnel. The smartphone is a viable device to meet this demand, as it is widely used and inexpensive, and has the necessary computation power and imaging technology [6]. In addition, PON devices have another major advantage related to their ecological characteristics, thanks to the low sample volume necessary to perform the analysis, the inclusion of the necessary reagents in the device and the use of

* Corresponding authors at: ECsens, Department of Analytical Chemistry, Campus Fuentenueva, Faculty of Sciences, University of Granada, 18071 Granada, Spain.
E-mail addresses: idorbe@ugr.es (I. Orbe-Payá), erenas@ugr.es (M.M. Erenas).

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ecological supports, such as paper, thread or cloth [7].

Over the last few years, different microfluidic devices have been proposed for the determination of sulfite in different beverages. The first, based on quenching a phosphorescent sensing membrane by sulfite, was included in a flow-injection analysis (FIA) system (LOD 10 μM) and applied to water and clear or turbid samples like vinegar or juice, but was not useful measuring sulfite in red wine[8]. Another example uses a microchip for the simultaneous determination of environmental samples of sulfite and nitrite after fluorescent derivatization (LOD 1 μM). Although the method represents a methodological simplification, a pumping systems is needed to make the reagents and sample flow through the system, which renders it non-portable and difficult to use [9]. More recently, several optical methodologies based on the use of smartphones or small homemade instrumentation have been applied to sulfite determination. Fatibello-Filho's group, for instance, proposes a digital image method based on the reduction of Fe(III) by sulfite and the complexation of Fe(II) with 1,10-phenanthroline (Phen) applied to white and rosé wine, as well as fruit juice (LOD 32 μM) [10]. Chen et al. have proposed a gas-diffusion μPAD using nano ZnO-paper disc in conjunction with surface-enhanced Raman spectroscopy (SERS) for sulfite determination in food and wines (LOD 25 μM) [11].

Recently, two paper have been published using headspace microextraction technique for separation of sulfite as SO_2 and its collection on cellulose paper impregnated with the ferric complex of Phen in one case [12] and on the head of a cotton swab with the same reagent in the second [13]. In both cases an homemade accessory is used to house a smartphone to acquire an image used for the development of a colorimetric method (LOD 0.5 μM [12] and LOD 1.5 μM [13]).

The elimination of interferents and colorants present especially in red wine is proposed in the literature using headspace techniques, which makes the procedure more complex and with a series of analytical operations.

As can be seen, the application of all these new optical methodologies to samples with intense colours such as red wine is extremely limited, due to the difficulty inherent in integrating the separation step of red wine dyes in the PON device while maintaining its simplicity. This work presents two capillary microfluidic devices based on thread (μTPAD) and paper (μPAD) designed to determine sulfite content without any type of pretreatment in different types of wine (red and white) based on selective sulfite recognition by means of a chromoreactand, in this case a formylazo dye (Fig. 1).

2. Materials and methods

2.1. Microfluidic device fabrication

2.1.1. μTPAD

The cotton thread used as the support was first scoured by boiling in an aqueous solution of 10 mg mL^{-1} Na_2CO_3 for 5 min to remove the thread waxes. The thread was then washed several times until the rinsate was pH neutral. Finally, it was sonicated 3 times in purified water for 5 min and left to dry at room temperature. To fabricate the μTPAD, 10 μL of pH 6.0 citric acid/citrate buffer 0.5 M was deposited at one end of a 20 mm long thread, previously stuck on double-sided adhesive tape and left to dry at room temperature for a few minutes. Then, a round piece of 2.5 mm diameter of sulfite sensor paper was attached to the other end of the thread. The prepared devices were stored in the dark until use.

2.1.2. μPAD

This device was made up of a sampling area, separation area, sensor paper and a passive pump. The sampling and separation area was prepared using 1248 Filter-Lab paper (basis weight 80 g m^{-2}; thickness 0.210 mm; retention 25–30 μm) previously laminated on one side with bioriented polypropylene (BOPP) lamination film at 100 °C. Once

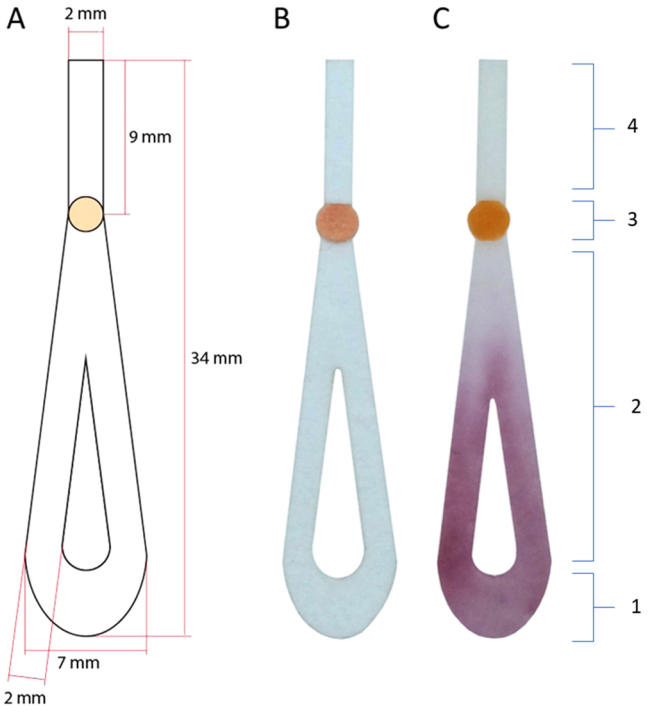

Fig. 2. A: μPAD double channel design with sampling area (1), separation area (2), sensor paper (3) and passive pump (4). B: μPAD before being used. C: μPAD after being used for red wine sample.

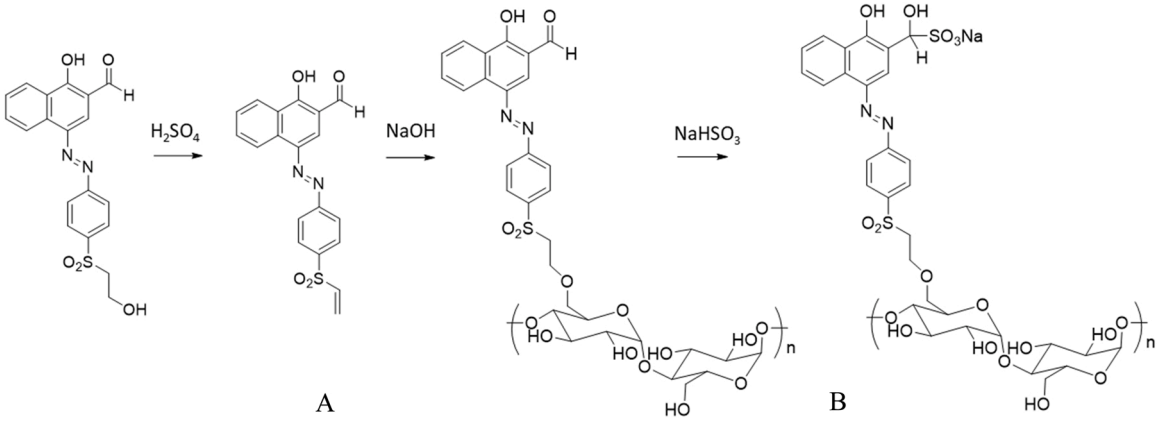

Fig. 1. A: Covalent immobilization of GJM-530 on cellulose paper; B: Sulfite reaction with GJM-530.

laminated, the paper was used as an input material for a cutting plotter (speed: 60 mm s^{-1}; force: 75 g), which cut the dual-channel shape (Fig. 2). Then, 0.5 μL of pH 6.0 citric acid/citrate buffer 0.5 M were added to a round piece (2.5 mm) of sensor paper, which was left to dry. This round piece was then attached to the end of the separation area (Fig. 2), which was stuck to a piece of double-sided adhesive tape. A 2 × 9 mm non-laminated rectangular piece of the same paper was placed at the end of the sensor paper as a passive pump (Fig. 2 and Fig. S14). The prepared devices were stored in the dark until use.

2.2. Image capture and processing

Both the μTPAD and μPAD were imaged after reacting with sulfite with a Sony DSC-HX300 camera located in a fixed position in a cubic light box to maintain the image acquisition conditions constant and isolated from external radiation. For still images, the camera was set up as follows: 3648 × 2736 pixel resolution, f/4 aperture value, 1/40 s exposure time, ISO 80, 5600 K white balance (see Section S2). The captured images were saved in jpg format (Joint Photographic Experts Group). For video recordings, the camera was set up as follows: 1440 × 1080 pixel resolution, 25 frames per second, and 5000 K white balance, and the file was saved in MTS (AVCHD) format. The image and video obtained were analysed using ImageJ and Avidemux software to select the region of interest (ROI) of the devices.

2.3. Analytical protocol

To determine the sulfite, 10 μL in the case of μTPAD and 20 μL for μPAD of the sample was deposited in the sampling area of the device. After 1 min, the reaction was complete, with the orange colour in the sensor paper changing to yellow (Fig. 2). Then, an image from the device was captured using a digital camera, as described above, and the hue (H) chromatic coordinate of the ROI was calculated. The sulfite concentration was calculated from the calibration function obtained with the standards. All the sulfite standards were prepared by dilutions from a 0.1 M $NaHSO_3$ stock solution that was prepared daily and standardized by iodimetric titration, using As_2O_3 as the primary standard [4]. Wine samples were analysed for sulfite without any pretreatment by dropping 10 μL of white wine samples onto the μTPAD sampling area or 20 μL of red or white wine in the case of the μPAD. Each wine was analysed in triplicate with the proposed devices and by iodimetric titration, and the results were compared in terms of percentage of error.

3. Results and discussion

A typical example of carbonyl additions – a π bond addition reaction – is the addition of sulfite, which occurs quickly with most aldehydes with no need for a catalyst, due to the efficient nucleophilic character of sulfite. Sulfite forms adducts by a reversible reaction with the aldehydes and ketones present in many food components, naturally or intentionally as an additive, giving rise to the formation of α-hydroxysulfonates, which accounts for most of the bound sulfite, at a pH between 1 and 8, with dissociation occurring at a higher pH (sulfurous acid: pK_1 1.81; pK_2 6.91) [14,15] (Fig. 1).

We propose using this reaction to determine sulfite based on a formylazo dye interaction, which changes the electron acceptor strength of the dyes and, consequently, their colour. This concept – the use of specific indicator dyes immobilized in polymeric layers that undergo a reversible chemical reaction with the analyte modifying their optical characteristics [16–19] – was developed by G. Mohr under the name chromoreactand.

The formylazo dye prepared as the reagent for sulfite is 4-[4-(2-hydroxyethanesulfonyl)-phenylazo]−2-formylnaphthalen-1-ol (GJM-530), synthesized and characterized by us (see SI-3 and SI-4). To develop the microfluidic devices, the GJM-530 reagent was covalently linked to paper by vinyl sulfone chemistry. The cellulosic membrane was used as a sensor paper that turns from orange to yellow in the presence of sulfite.

3.1. Characterization of the immobilized chromoreactand

Once the GJM-530 reagent was immobilized in Whatman 1 paper (see Section S5), it was necessary to characterize it as a reagent in terms of the analytical parameter, working pH and reversibility. To that end, 2.5 mm diameter discs of the sensor paper were dipped for two min. in ten different sulfite solutions buffered at a fixed pH using 1 M citric acid/citrate buffer (see Section S6), and then digitized.

To choose the colour coordinate to be used as an analytical parameter (see Section S6), different sensor papers were reacted with different sulfite solutions. Figs. S4 and S5 show that the H parameter is the colour coordinate with the highest signal variation and the lowest error bars.

The influence of pH on the reaction was tested using sulfite solutions buffered at pH 4.0, 4.9, 6.0 and 7.0. Fig. S6 shows that pH 6 causes the greatest variation in H, and better precision, and was thus chosen as the working pH. Additionally, at that value hydrogensulfite is the predominant species.[2].

Finally, the reversibility of the sensor paper was studied by subjecting it to an increasing concentration of sulfite and, subsequently, to decreasing concentrations. Fig. S7 shows how the sensor paper only recovers 43% of the signal when successively immersed in solutions of increasing and decreasing sulfite concentration.

Although it has been described that this type of chromoreactand is reversible in solution, [16] the immobilization on paper, the formation of a hydrogen bond in the hydroxy-naphthalene group that stabilizes the structure or the high chemical reactivity of the dye could be the reason for the partial irreversibility observed with the sensor paper.

3.1.1. μTPAD optimization

As the material to make the capillary platform, we selected commercial cotton thread in combination with paper to implement all the necessary analytical operations: sampling, pretreatment and recognition of the sulfites. The μTPAD designed for the determination of sulfites was a 20 mm long cotton thread with a circular sensor paper at its end. To obtain reproducible signals, as well as to simplify the measurement procedure, the influence of the sample volume, the reaction time of the sulfite recognition reaction and the buffering of the sample in the device were studied.

To study the sample volume to use, the minimum volume of liquid necessary to homogeneously wet the sensor paper was studied first (Section S7.1); this value was 9 μL. The sample volume was then studied to obtain the maximum signal compared to the value by immersion; 10 μL was the volume selected (see Section S7.1).

Once the sample volume was selected, the time required to obtain a stable signal was studied. It was found that 60 s is sufficient to generate a constant value of the parameter H (See Section S7.2).

The pH adjustment step was performed on the μTPAD device itself to avoid sample pretreatment. For this, 10 μL of pH 6.0 citric acid / citrate buffer 0.5 M was deposited directly on the μTPAD thread, which was allowed to dry under ambient conditions. Fig. S12 shows that the signals obtained with immobilized buffer and buffer in solution are similar, and consequently, there is no need to adjust the pH in solution prior to measurements.

In order to optimize the minimum amount of reagents and materials, the size of the circular sensor paper was studied by testing circles 2, 2.5 and 3 mm in diameter (Fig. S13). The 3 mm diameter sensor paper shows the lowest H variation (0.0416) and was not used for further studies. Of the 2.0 and 2.5 mm diameter circles, 2.5 mm was chosen because it presented the lowest CV, with 3.04% compared to 4.95% for 2 mm.

3.2. Calibration and analytical parameters

After optimization of the different variables, the μTPAD was

analytically characterized. To this end, nine different sulfite solutions ranging from 10^{-5} to 10^{-1} M were used, obtaining the signal 60 s after adding the sample. For this study, 27 μTPAD's (n = 3) were used and the H value obtained was adjusted to a Boltzmann equation against the logarithm of the sulfite concentration Eq. (1).

$$y = A_2 + \frac{(A_1 - A_2)}{1 + e^{\frac{(x-A_3)}{A_4}}} \quad (1)$$

Fig. 3 shows the evolution of H experimental data from μTPAD as well as its fit to a sigmoidal Boltzmann equation with a R^2 of 0.994. Figures of merit (See Table 1) of the μTPAD were calculated obtaining a CV lower than 5% (n = 5) and a limit of detection (LOD) of 78 μM. Finally, the range of application of the μTPAD was found to be from $7.8{\cdot}10^{-5}$ M (8.1 mg L^{-1}) to 2.7 10^{-3} M (279.3 mg L^{-1}).

3.3. Study of interferences

The possible interference of different major compounds present in wines was studied, including lactic, acetic and tartaric acids, alcohols like ethanol and sugars such as fructose, glucose and sucrose. The acids and ethanol concentrations tested were close to the maximum concentration found in wine: 1 g L^{-1} of acetic acid, 3 g L^{-1} of lactic acid, 5 g L^{-1} of tartaric acid, 40 mg L^{-1} cysteine, 100 mg L^{-1} glutathione and a 13% (v/v) of ethanol, and compared to the signal obtained from a blank and also from a 1.0 mM sulfite solution (Fig. 4a). No interferences from these compounds were found. The sugars were tested at three different concentrations, and the results were compared with the signal obtained at a 1.0 mM sulfite concentration (Fig. 4c), as well as with mixtures of sulfite (1.0 mM) and sugars (67.5 mg L^{-1}) (Fig. 4b). The results obtained from this study concluded that the presence of these compounds does not interfere with the signal from sulfite.

Table 1
Figures of merit from the μTPAD and μPAD for sulfite determination.

Parameter	μTPAD	μPAD
A_1	0.04811	0.05153
A_2	0.14313	0.1466
A_3	-3.381	-2.8574
A_4	0.42116	0.35816
R^2	0.994	0.998
LOD	$7.8{\cdot}10^{-5}$ M	$2.2{\cdot}10^{-4}$ M
Dynamic Range	$7.8{\cdot}10^{-5}$ to $2.7{\cdot}10^{-3}$ M	$2.2{\cdot}10^{-4}$ to $8.9{\cdot}10^{-3}$ M
Average precision (n = 5)	3.0%	2.6%
Analysis time	60 s	60 s
Sample	White wine (10 μL)	Red/white wine (20 μL)

The μTPAD method was successfully applied to seven white wines from different Spanish wine regions. 10 μL of sample was added to the

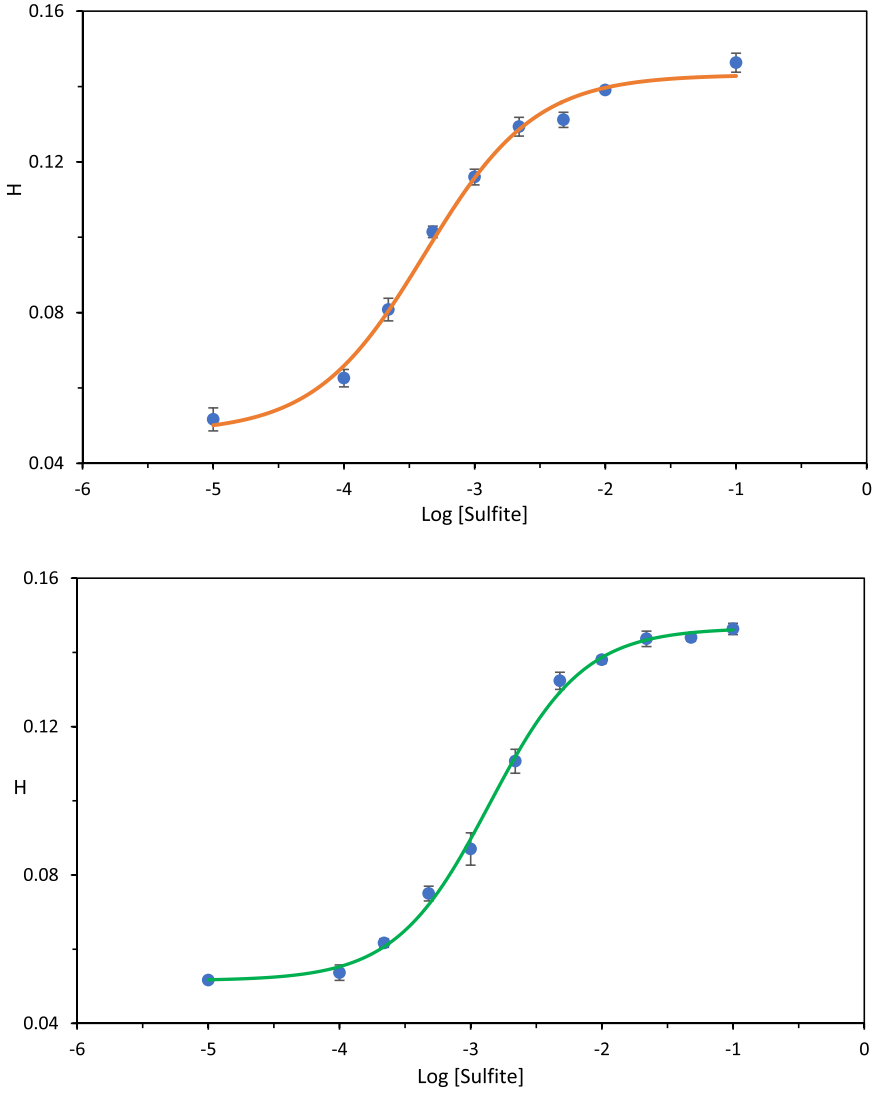

Fig. 3. Calibration function and experimental data obtained from μTPAD (upper graph) and μPAD (lower graph).

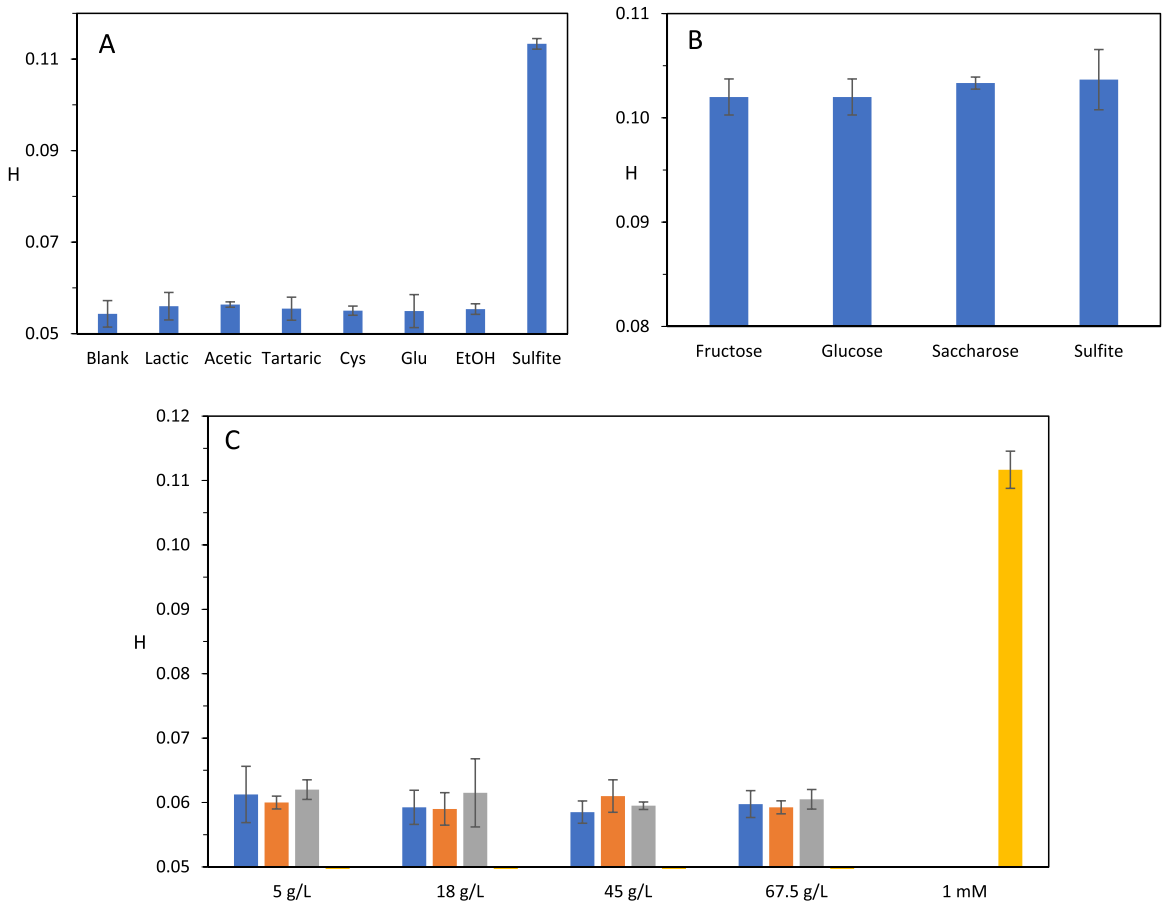

Fig. 4. A: H values obtained in μTADs for 3 g L^{-1} lactic acid, 1 g L^{-1} acetic acid, 5 g L^{-1} tartaric acid, 40 mg L^{-1} cysteine, 100 mg L^{-1} glutathione and 13% (v/v) of ethanol solutions and a 1 mM sulfite solution. B: H values obtained in μTADs for sugar solutions at 67.5 mg L^{-1} and 1 mM sulfite compared with 1 mM sulfite solution. **c** H values obtained in μTADs for 5, 18, 45 and 67.5 g L^{-1} fructose (blue), glucose (orange) and saccharose (grey) compared to 1 mM sulfite solutions (yellow).

device, obtaining errors ranging from 3% to 19% (see Table 2) when compared with the results obtained from the iodimetric titration [4].

3.4. Sulfite determination in red wine

The intense colour of red wine is mainly due to the pigments present in grapes, especially different phenolic compounds like anthocyanins that are transformed, during the wine aging process, into more stable structures such as pyranoanthocyanins[20]. The presence of these pigments means that the μTPAD device cannot be used due to the red coloration that the sensor paper takes from the sample, which interferes with the colorimetric measurement.

Table 2
Validation of μTPAD and μPAD using commercial wine samples.

Sample	Kind	Designation of origin	μTPAD Sulfite mg L^{-1}	Iodimetric titration Sulfite mg L^{-1}	IErrorI
1	White	Rioja	39.4	42.0	6%
2	White	Rueda	42.6	43.1	1%
3	White	La Mancha	32.2	32.8	2%
4	White	Rioja	57.6	57.0	1%
5	White	Rueda	51.4	57.6	11%
6	White	Uriel-Requena	31.7	39.2	19%
7	White	Valencia	27.7	26.6	4%
Sample	**Kind**	**Designation of origin**	**μPAD Sulfite mg L^{-1}**	**Iodimetric titration Sulfite mg L^{-1}**	**IErrorI**
8	Red	Rioja	27.5	33.9	19%
9	Red	Uriel-Requena	28.5	29.1	2%
10	Red	Rioja	24.0	20.3	18%
11	Red	Ribera del Duero	20.1	23.9	16%
12	Red	Rioja	29.6	27.4	8%
1	White	Rioja	37.6	42.0	10%
5	White	Rueda	52.2	57.6	9%

To determine sulfites using a colorimetric PON device, a prior decolorization of the wine sample was required, without affecting the sulfite content present, so that the solution that reached the sensor area was colourless. To separate the colorants from the red wine, the introduction of a separation step using filter paper in the device was proposed. To perform the separation, seven different types of paper were cut into 3 mm × 70 mm strips and deposited on a double adhesive tape; then 10 μL of different types of red wine were deposited on one end and a digital image was taken after five minutes. As a parameter to measure the efficiency of the separation, W_R, was defined as the quotient between the length of the discoloured area of the paper and the total distance travelled by the wine sample (see Table S3).

The papers in references 1248 and 1249 provide the best separation. To select the most appropriate, the reproducibility of the separation process (n = 10) was studied, finding that paper 1248 presented a value of 6.9%, compared to 11.6% for 1249, which is why the 1248 paper was selected as the best support for μTAD in terms of separation and reproducibility.

The width of the separation channel was studied by testing widths of 1, 2 and 3 mm. The 1 mm wide paper was rejected as having low stability. The 2 mm channel produced a better separation (W_R = 0.428) than the 3 mm channel (W_R = 0.395), so that size was selected.

In order to increase the separation performance of the colorants present in the wine and also improve the physical properties of the paper (wetness stability, consistency, rigidity), the lamination of the device was studied. 2 mm × 70 mm paper strips, unlaminated, laminated on one side, and laminated on both sides were tested using 10 μL of red wine. The double lamination of the paper improved the separation process (W_R 0.641); even single-sided lamination had a better factor (W_R 0.507) than non-laminated paper (W_R 0.432). Both laminated papers also improved the mechanical properties, presenting greater resistance to wetting.

The amount of the wine sample used to separate the dyes, studied in the range 7.5–12.5 μL, kept the separation factor constant (7.5 μL, W_R = 0.402; 10 μL, W_R = 0.405; 12.5 μL, W_R = 0.404) and the separation was not affected in this volume range.

Finally, due to the separation process performed in the separation channel, it was not possible to drop the buffer into the separation channel as was described for the μTPAD, because the presence of the dry buffer affected the separation process negatively. Therefore, the buffering process was done directly on the sensor paper by adding 0.5 μL of 0.5 M of citric acid / citrate pH 6 buffer (see Section 8.3).

3.5. Calibration of μPAD for sulfite

Once the μPAD was optimized, it was calibrated (see Section 8.4), but the analytical parameters obtained in terms of LOD (233 mg L^{-1}) made it impossible to use in real wine samples, because the highest sulfite concentration allowed is in the range from 150 to 500 mg L^{-1}, depending on the kind of wine. The reason for the low signal obtained, is because only a low volume of the sample reaches the sensor paper. This is due to the fact that a high volume of sample is absorbed by the paper support, compared to thread.

If a higher amount of the colourless wine sample can wick to the sensor paper, it could be possible to obtain a higher signal at lower sulfite concentration. Unfortunately, it was not possible to simply increase the amount of the sample, because this also affected the separation process of the colorants from the sensor paper. For this reason, a new μPAD was designed, with the single 2 × 21 mm channel replaced by a double channel laminated on only one side. This made it possible to add 20 μL of the sample instead of 10 μL and to increase the amount of the decolorized sample that reached the sensor paper (Fig. 2). Moreover, a passive pump at the end of the device composed of a piece of 2 × 9 mm paper allowed a higher volume of sample to wick along the sensor paper.

The calibration of the bi-channel device was adjusted to a Boltzmann equation with 0.998 of R^2. The changes made including the passive pump, one sided laminate and bi-channel design improved the signal significantly (see Fig. 3), obtaining an LOD of $2.2{\cdot}10^{-4}$ M (22.7 mg·L^{-1}) and a CV (n = 5) of 2.6% (see Table 1). Accordingly, this approach now performs well for red wine.

3.6. Wine samples

The μPAD was used to determine sulfite concentration in white and red wine, obtaining the results shown in Table 2 and compared to a reference method, iodimetric titration. As can be observed, red and white wines from different designations of origin were successfully analysed, when compared with the reference method. The error calculated for the determination of the samples ranged from 1% to 19%.

4. Conclusion

This study presents two PON devices that permit the determination of sulfite in wine. The first approach was a μTPAD that permits to perform the determination in white wine where the colorants are not going to interfere in the colorimetric signal obtained but being not possible its application to red wines. To avoid this limitation, a second device where paper was used as support μPAD was developed. The use of paper makes possible to separate the colorants in red wine from the sulfites that reach the sensor paper.

This separation prevents the coloration of the sample from interfering with the colorimetric signal obtained and, thus, affecting the determination of sulfite and allowing it use on red and white wines.

Additionally, the use of GJM-530 chromoreactand immobilized on the sensor paper via covalent bond improves the reproducibility of the μPAD, preventing leaching from the paper to the sample, and making it possible to obtain a selective signal from a complex matrix sample, like white and red wine.

The μPAD allows for sulfite determination in the range of $2.2{\cdot}10^{-4}$ to $8.9{\cdot}10^{-3}$ M in 60 s using 20 μL of the sample, and obtaining a precision around 2.6%. The results obtained when applied to 12 different wine samples were compared to a reference method, demonstrating the utility of the sensor. Additionally, the proposed method is environmentally-friendly, using a low volume of reagents and sample and generating very little waste, all of which demonstrates the potential of this kind of device in the agro-food industry.

CRediT authorship contribution statement

Manuel J. Arroyo: Investigation, Validation, Formal analysis, Writing – original draft. **Ignacio de Orbe-Payá:** Validation, Supervision, Methodology, Formal analysis. **Mariano Ortega-Muñoz:** Resources, Characterization, Formal analysis. **Jose Vilar-Tenorio:** Investigation. **David Gallego:** Investigation, Software, Conceptualization. **Gerhard J. Mohr:** Synthesis, Resources, Writing – original draft. **Luis F. Capitán-Vallvey:** Validation, Writing – original draft, Resources, Writing – review & editing, Project administration, Funding acquisition. **Miguel M. Erenas:** Conceptualization, Validation, Formal analysis, Writing – original draft, Writing – review & editing, Supervision.

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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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.snb.2022.131549.

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Manuel Jesús Arroyo received the Major degree in Pharmacy from de University of Granada (Granada, Spain) in 2017. In the next year (2018) received the Masterś degree in Research, Development, Control and Innovation of drugs in the same University. He is currently pursuing the Ph.D degree at the ECSens Group, Department of Analytical Chemistry, University of Granada. His research interests include the design and characterization of microfluidic capillary diagnostic devices.

Ignacio de Orbe-Payá is Associate Professor of the Department of Analytical Chemistry at the University of Granada (Spain). His main areas of research are the development of the sensing phases for their use as chemical sensors in the determination of inorganic ions in several matrices; multivariate calibration methods for the quality control of pharmaceutical products and development of analytical methodology using solid-phase spectrometry.

Mariano Ortega Muñoz, received the MSc degree (2002) and the Ph.D. degree in Organic Chemistry (2007) from the University of Granada (Granada, Spain). Currently he works as Associate Professor at the University of Granada. He is a member of the "Glycochemistry & Bioconjugation" (GlycoChemBio) research group and his current research interests are focused in the development of new synthetic methodologies based in "click-chemistry" reactions and their applications in diverse areas: cyclodextrins, drug delivery, non-viral gene transfection, carbon nano-materials, labeling and immobilization of biomolecules.

Jose Vilar Tenorio is a bachelor's degree holder interested in the development of capillary based microfluidic devices.

David Gallego is a technician from the ECsens research group, expertise in 2D/3D design and printing.

Gerhard J. Mohr received his Ph.D. in Chemistry (1996) at Karl-Franzens University Graz in the field of optical sensors for anions. Then he moved to the Centre for Chemical Sensors at ETH Zurich where he was engaged in the synthesis and characterisation of new chemosensor dyes and functional polymers. In May 2001, he submitted his habilitation thesis entitled: "Chromogenic and fluorogenic reactands: New tools for molecular recognition of neutral analytes" to the Department of Applied BioSciences of the Swiss Federal Institute of Technology (ETH) and received the Venia Legendi in April 2002. From 2001 until 2008, he was Marie Curie and Heisenberg fellow at Friedrich-Schiller University Jena and from 2009 until 2011 he was establishing the Fraunhofer workgroup Sensor Materials in Regensburg, focussing on new functional dyes, fluorescent nanosensors and their combination with polytronic systems. Currently, he is senior researcher at Joanneum Research, developing new indicator dyes for polymer layers, textiles and non-wovens and combining them with information and communication technology.

Luis Fermín Capitan-Vallvey, Full Professor of Analytical Chemistry at the University of Granada, received his B.Sc. in Chemistry (1973) and Ph.D. in Chemistry (1986) from the Faculty of Sciences, University of Granada (Spain). In 1983, he founded the Solid Phase Spectrometry group (GSB) and in 2000, together with Prof. Palma López, the interdisciplinary group ECsens, which includes Chemists, Physicists and Electrical and Computer Engineers at the University of Granada. His current research interests are the design, development and fabrication of sensors and portable instrumentation for environmental, health and food analysis and monitoring. Recently is interested in printing chemical sensor and capillary-based microfluidic devices.

Miguel Maria Erenas received the M.Sc. degree (2004) and the Ph.D. degree in Analytical Chemistry (2011) from the University of Granada (Granada, Spain). He is currently working as a Researcher at the ECsens group, Department of Analytical Chemistry, University of Granada and his research interests include the use of imaging along with microfluidic disposable sensors based on thread and paper for bioanalysis and food quality analysis.