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Determination of total sulfite in wine Zone electrophoresis–isotachophoresis quantitation of sulfate on a chip after an in-sample oxidation of total sulfite

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Abstract

This work deals with the determination of total sulfite in wine. The determination combines an in-sample hydrogen peroxide oxidation of total sulfite in alkalized wine to sulfate with the separation and quantitation of the latter anion by zone electrophoresis (ZE) on-line coupled with isotachophoresis (ITP) on a column-coupling chip. Sample clean up, integrated into the ITP–ZE separation, eliminated wine matrix in an extent comparable to that provided by a highly selective distillation isolation of sulfite. At the same time, conductivity detection, employed to the detection of sulfate in the ZE stage of the ITP–ZE combination, provided for sulfate the concentration limit of detection corresponding to a 90 μg/l concentration of sulfite in the loaded sample (0.9 μl). Such a detectability allowed a reproducible quantitation of total sulfite when its concentration in wine was 15 mg/l. Formaldehyde binding of free sulfite in wine, included into the pre-column sample preparation, prevented an uncontrolled oxidation of this sulfite form. This step contributed to an unbiased determination of sulfate present in the original wine sample (this determination corrected for the concentration of sulfate determined in the sample after the peroxide oxidation of sulfite to the value equivalent to the total sulfite). The 99–101% recoveries of sulfite, determined for appropriately spiked wine samples, indicate a very good accuracy of the present method. Such a statement also supports excellent agreements of the results of quantitation based on the in-sample peroxide oxidation of the total sulfite (bound sulfite released at a high pH) with those in which this analyte was isolated from wine by distillation (bound sulfite released at a very low pH).

Keywords: Electrophoresis on chip; Zone electrophoresis–isotachophoresis chip; Sulfite in food; Food analysis; Wine analysis

1. Introduction

The use of sulfur dioxide and/or oxoanions of S(IV) in the vinification process is essential [1,2]. Sulfite added to wine forms with wine constituents numerous products during this process [3–6]. Of these, for example, adducts of sulfite with carbonyl groups of some wine constituents are responsible for the fact that a part of sulfite is present in wine in a reversibly bound form. These adducts decompose on acidification or alkalization of wine and release a corresponding amount of sulfite.

Contents of free sulfite and total sulfite in wine characterize its quality and they are routinely determined (as individual analytical parameters) in winery laboratories [7–9]. Analytical methods recommended to the determination of total sulfite in wine usually employ Monier-Williams distillation method to selectively isolate sulfite [10–12] before its oxidation to an equivalent amount of sulfate (sulfuric acid). One of the numerous modifications of the Monier-Williams distillation method can be employed in the quantitation of both free and reversibly bound sulfite in wine [12]. In this instance, differ-

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ent temperatures at which sulfur dioxide is released from the acidified wine sample provide means for defined isolations of these forms.

The distillation step may be considered a bottleneck of the analytical methods used in the determination of (total) sulfite in food and attempts aimed at its elimination are apparent (see [9,13–22]). For example, when wine is alkalized the reversibly bound sulfite is released [3–6] and can be immediately oxidized to sulfate by hydrogen peroxide. As shown recently by Edmond et al. [14], this approach, combined with ion chromatography quantitation of sulfate, makes possible the determination of total sulfite in wine.

Recently, we developed a method of the determination of free sulfite in wine using zone electrophoresis (ZE) with on-line coupled isotachophoresis (ITP) sample pretreatment (ITP–ZE) on a column-coupling (CC) chip with integrated conductivity detection [17]. This simple method, including a rapid conversion of free sulfite to hydroxymethanesulfonate (HMS), is suitable to the determination of free sulfite in wine in about 10 min.

The present work was aimed at developing a CC chip based method applicable to the determination of total sulfite in wine. To keep the sample handling at a minimum, we favored the use of an in-sample oxidation of both the free and bound forms of sulfite by hydrogen peroxide at a high pH [14]. The ITP–ZE determination of sulfate formed in this way, corrected for the content of sulfate present in the original sample, served as a measure of the total content of sulfite. Developments of suitable ITP–ZE separating conditions along with a search for optimum conditions for hydrogen peroxide oxidation of sulfite in wine were main tasks of this work.

2. Experimental

2.1. Instrumentation

A schematic arrangement of channels on a poly(methylmethacrylate) CC chip used in this work along with geometrical dimensions of the channels are given in Fig. 1. This chip was made in the laboratory using fabrication procedures described elsewhere [23]. The separations in this miniaturized device were performed with the aid of a laboratory constructed electrophoresis equipment (see [17,24] for its description). The conductivity sensors on the chip (see Fig. 1) were galvanically decoupled [25] from the measuring circuitry of the equipment by miniature transformers.

MicroCE Win software (version 2.4), written in the laboratory, controlled automated preparations of the runs (filling the chip channels with the corresponding solutions in a required sequence), provided a time-programmed control of the ITP–ZE runs (including the column-switching operation during the run derived from the signal of the conductivity detector in the ITP channel; Fig. 1), acquired the detection data and provided their processing.

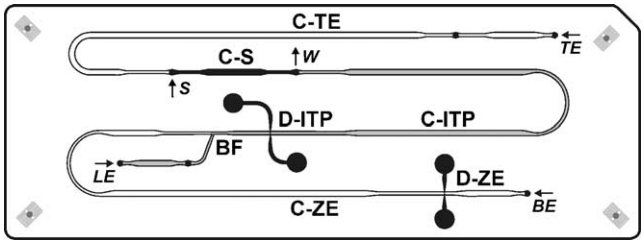

Fig. 1. An arrangement of the channels on a poly(methylmethacrylate) CC chip and the channel dimensions. C-TE: terminating electrolyte channel (9.8 μl volume; 60 mm × 0.2–0.5 mm × 0.2–0.38 mm [length × width × depth]); C-S: sample injection channel (0.9 μl volume; 12 mm × 0.2–0.5 mm × 0.2 mm); C-ITP: ITP separation channel (4.5 μl volume; 59 mm × 0.2–0.5 mm × 0.14–0.2 mm) with a platinum conductivity sensor (D-ITP); C-ZE: ZE separation channel (4.3 μl volume; 56 mm × 0.2–0.5 mm × 0.14–0.2 mm) with a platinum conductivity sensor (D-ZE); BF: bifurcation section; BE, LE, TE and S: inlets for the background (carrier), leading, terminating and sample solutions to the chip channels, respectively; W: outlet for the solutions from the chip channels.

2.2. Chemicals and electrolyte solutions

Chemicals used for the preparation of the electrolyte solutions and the solutions of model samples were obtained from Merck (Darmstadt, Germany), Sigma–Aldrich (Seelze, Germany) and Serva (Heidelberg, Germany). Some of them (hydrochloric acid and β-alanine) were purified by conventional purification methods [26]. Methylhydroxyethylcellulose 30 000 (Serva), purified on a mixed-bed ion exchanger (Amberlite MB-1, Merck), was used as a suppressor of electroosmotic flow. Added to the electrolyte solutions (Table 1), this cellulose derivative dynamically coated the inner walls

Table 1
Electrolyte system

ITP		ZE	
Leading anion	Chloride	Carrier anion	Citrate
Concentration (mmol/l)	10	Concentration (mmol/l)	15
Counter ion	β-Alanine	Counter ion	β-Alanine
Concentration (mmol/l)	4	Concentration (mmol/l)	11.8
Co-counter ion	Bis–tris propane	Co-counter ion	Bis–tris propane
Concentration (mmol/l)	4	Concentration (mmol/l)	7
EOF suppressor	MHEC[a]	EOF suppressor	MHEC[a]
Concentration (%, w/v)	0.05	Concentration (%, w/v)	0.2
pH	3.5	pH	4.0
Terminating anion	Citrate		
Concentration (mmol/l)	20		
Counter ion	β-Alanine		
Concentration (mmol/l)	30		
EOF suppressor	MHEC[a]		
Concentration (%, w/v)	0.05		
pH	3.5		

[a] MHEC: methylhydroxyethylcellulose.

of the chip channels [27]. Compositions of the electrolyte solutions employed in the ITP–ZE separations are given in Table 1. The solutions were stored at +4 °C and filtered by disposable membrane filters (a 0.8 μm pore size; Millipore, Molsheim, France) before the use.

Water demineralized by a Pro-PS water purification system (Labconco, Kansas City, KS, USA) and kept highly demineralized by a circulation in a Simplicity deionization unit (Millipore), was used for the preparation of the electrolyte and sample solutions.

A stock aqueous solution of sodium sulfite (Merck) was prepared fresh daily, while the stock solution of its complex with formaldehyde (HMS), corresponding to a 1000 mg/l concentration of sulfite in a 10 mmol/l formaldehyde, was stable, at least, for 1 week when stored at +4 °C. Sodium sulfate (Titrisol, Merck), when appropriately diluted, served as a reference analyte in our experiments.

2.3. Samples and pre-column sample preparation

Several white and red wines of various geographical origins, bought in a local wine shop, were used in preliminary experiments performed in a context of this work. White wine, Műller Thurgau (year 2002; Vinárske závody, Topol'čianky, Slovak Republic) bought in a local wine shop and red wine, Heppenheimer Centgericht Spätburgunder (year 1999; Staatsweingut Bergstrasse, Bensheim, Germany) kindly provided by Dr. Dieter Tanzer (Merck, Darmstadt, Germany) served as samples in final developments of the procedures described in this work.

2.3.1. Formaldehyde stabilization of free sulfite in wine [17]

The sample, immediately after bottle opening, is diluted in a 10 ml volumetric flask in an aqueous solution containing formaldehyde (corresponding to a 10 mmol/l final concentration of formaldehyde) and the terminating electrolyte solution (corresponding to a 1 mmol/l final concentration of the terminating anion). The volume of wine taken corresponds to its 15-fold dilution. The solution is made up to the mark with freshly demineralized water. To guaranty a full conversion of free sulfite to HMS, the sample is analyzed or further processed ca. 60 min after the preparation.

A comparative sample (without formaldehyde) is prepared, in parallel, in the same way.

2.3.2. Hydrogen peroxide oxidation of total sulfite in wine

A required amount of either the stabilized sample (Section 2.3.1) or an unstabilized sample (taken immediately after the bottle opening) is diluted in a 10% (v/v) terminating electrolyte solution (Table 1) in a 10 ml volumetric flask. A 0.06% (v/v) aqueous solution of hydrogen peroxide and a 5 mmol/l sodium hydroxide solution are added immediately. Then, the volume is made up to the mark with deionized water. This mixture is allowed to react for 30 min to guaranty a quantitative conversion of sulfite to sulfate. pH of the reaction mixture should not decrease below 10 (at lower pH values the rate of oxidation decreases significantly). Sulfate formed is determined, after an appropriate dilution of the reaction mixture with the terminating electrolyte solution (Table 1), by ITP–ZE on the CC chip under the working conditions described further.

A comparative sample (without hydrogen peroxide) is prepared, in parallel, in the same way.

2.3.3. Isolation of total sulfite from wine by distillation

Thirty milliliters of a 0.5 mol/l solution of phosphoric acid is added to a 10 ml volume of the wine sample in a distillation flask. The acidified sample is distilled, under a gentle stream of argon, on a steam bath for 1 h. Sulfur dioxide released from the sample is trapped into a 20 ml volume of 3% (v/v) hydrogen peroxide solution. Sulfate formed in the hydrogen peroxide solution is determined, after a 10-fold dilution of this solution with the terminating electrolyte solution (Table 1), by ITP–ZE on the CC chip under the working conditions described further.

3. Results and discussion

3.1. ITP–ZE separating conditions

As stated in Section 1, this work was aimed at developing a method suitable to the determination of total sulfite in wine in which an in-sample oxidation of sulfite to sulfate by hydrogen peroxide at a high pH,

$$SO_2 + H_2O_2 \rightarrow H_2SO_4, \quad (1)$$

is followed by the ITP–ZE quantitation of sulfate on the CC chip. Of the electrophoresis methods running on the CC chip [24], we favored ITP–ZE because this combination is, in general, effective in reaching rapid and reliable separation and quantitation of analytes present in complex ionic matrices (a typical feature of wine samples).

An operational scheme of the ITP–ZE run as shown in Fig. 2 was employed in the determination of sulfate on the CC chip. From this scheme, it is apparent that ITP focused sulfate present in the loaded sample into a narrow pulse between the leading and terminating zones (step b in Fig. 2). This concentration step made possible a low dispersion transfer of sulfate to the ZE channel of the chip (step c in Fig. 2). In addition, a low pH value at which the separation was performed and the use of very mobile terminating anion (Table 1) gave the sulfate transfer a high selectivity (only a very limited number of the anionic wine constituents could accompany sulfate in the ITP stack).

Differences in the actual ionic mobilities of chloride (the leading anion) and sulfate were critical in reaching a rapid ITP focusing of sulfate when the leading electrolyte (Table 1) contained only the pH buffering counter ion (β-alanine).

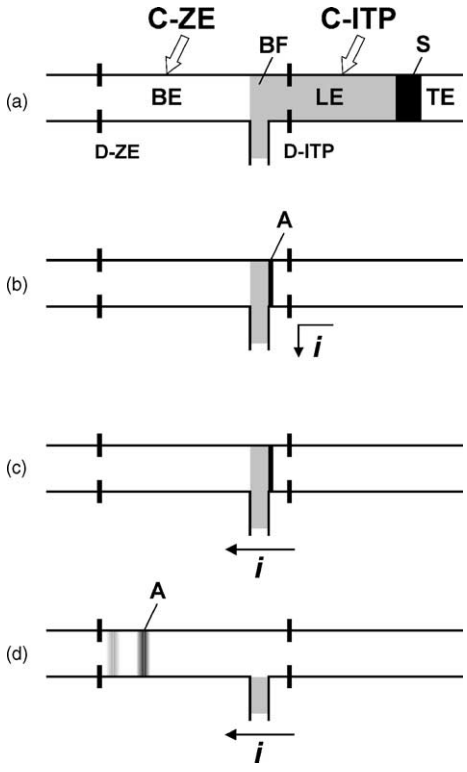

Fig. 2. A scheme of the ITP–ZE separation with a transfer of the constituents to the ZE channel on the CC chip. (a) An initial arrangement of the solutions in the chip channels; (b) end of the run in the ITP channel; (c) a transfer of the stacked sample constituents to the ZE channel by switching the direction of the driving current; (d) the separation and detection of the transferred sample constituents in the ZE channel. C-ITP and C-ZE: ITP and ZE separation channels on the CC chip, respectively; BF: bifurcation section; LE, TE and BE: the leading, terminating and background electrolyte solutions, respectively; S: sample; D-ITP and D-ZE: detection sensors in the ITP and ZE separation channels, respectively; *i*: direction of the driving current.

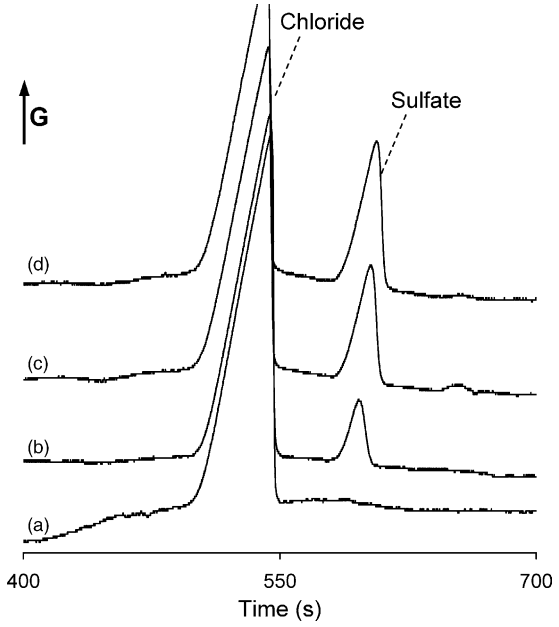

Fig. 3. Electropherograms from the ITP–ZE determination of sulfate formed by hydrogen peroxide oxidation of the total sulfite in a red wine sample (Heppenheimer Centgericht Spätburgunder): (a) a 10% (v/v) solution of the terminating electrolyte loaded [blank run]; (b) a 50-fold diluted wine sample with formaldehyde stabilized free sulfite; (c) the same sample as in (b) after hydrogen peroxide oxidation of the total sulfite; (d) the same sample as in (c), spiked with HMS at a 2 mg/l concentration before the peroxide oxidation. The separations were carried out in the electrolyte system given in Table 1. The driving current was stabilized at 30 μA in both channels. Chloride: the leading anion transferred with the sulfate pulse to the ZE channel (see step c in Fig. 2); G: increasing conductance.

Using bis–tris propane (a double charged cation at pH 3.5) as a co-counter ion in the leading electrolyte, we eliminated this resolution problem in a known way [28].

The ZE separation (destacking) of sulfate from the constituents present in the sample pulse transferred to the ZE channel started immediately after the column switching (step c in Fig. 2). The composition of the background (carrier) electrolyte employed in this channel (Table 1) reflected, besides the resolution of sulfate from the transferred matrix constituents, also adequate sulfate detectability by the conductivity detector [29,30].

Electropherograms in Figs. 3 and 4 illustrate a separation performance of the ITP–ZE combination as attained on the CC chip under the separating conditions developed in this work. A high selectivity in the ITP–ZE determination of sulfate is apparent from these electropherograms. They show that ITP provided for sulfate sample clean up (Fig. 3) comparable to the one characterizing a highly selective distillation isolation of sulfite (Fig. 4).

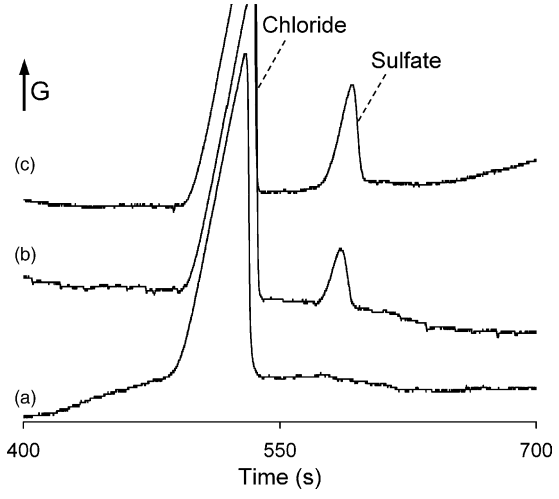

Fig. 4. Electropherograms from ITP–ZE determination of sulfate formed by hydrogen peroxide oxidation of total sulfite isolated from a red wine sample (Heppenheimer Centgericht Spätburgunder) by distillation: (a) a 10% (v/v) solution of the terminating electrolyte [blank run]; (b) a 20-fold diluted solution of hydrogen peroxide in which the isolated sulfite was trapped; (c) the same sample as in (b), spiked with sulfite (in the HMS form) at a 40 mg/l concentration before the distillation; a 20-fold diluted solution of hydrogen peroxide in which the isolated sulfite was trapped was loaded on the chip. See the caption of Fig. 3 for further details.

Table 2
Repeatabilities of the migration times and peak areas of sulfate formed by hydrogen peroxide oxidation of sulfite present in model samples

Concentration of sulfite (mg/l)	ITP pretreatment time (s)[a]		Migration time in ZE stage (s)[b]		Peak area (mV s)		n[c]
	Mean	S.D.	Mean	S.D.	Mean	S.D.	
2[d]	259	1.1	335	1.0	40.9	0.4	10
4[e]	258	1.9	339	3.5	81.3	1.8	25
8[d]	258	0.9	343	2.0	166.1	2.0	10

The separations were carried out in the electrolyte system given in Table 1. The driving current was 30 μA in both channels.
[a] A time of entrance of the sulfate zone to the bifurcation section of the CC chip (BF in Fig. 2).
[b] A migration time of sulfate in the ZE stage.
[c] n: number of repeated ITP–ZE runs.
[d] ITP–ZE runs were performed with a particular model sample (sulfite bound in HMS was oxidized) in 1 day.
[e] ITP–ZE runs were performed in 5 days (each day a new HMS sample was oxidized).

3.2. Quantitation of total sulfite in wine

Following the work of Edmond et al. [14], we carried out hydrogen peroxide oxidation of the free and bound forms of sulfite in wine at pH ≈10. Moreover, to prevent an uncontrolled oxidation of free sulfite on sample handling, we included into the pre-column sample preparation a rapid and, at the same time, quantitative formaldehyde conversion of free sulfite to hydroxymethanesulfonic acid [17]:

$$SO_2 + HCOH + H_2O \rightarrow HOCH_2SO_3H. \quad (2)$$

Such a stabilization of the analyte, performed immediately after the bottle opening in the way described in Section 2, was assumed to have no adverse effect on a completeness of sulfite oxidation. Experiments performed in this context with model samples revealed that the HMS bound sulfite was oxidized by hydrogen peroxide quantitatively (see Tables 2 and 3). Similar conclusions can be drawn from the data as obtained for wine samples (see further).

The time required for a complete oxidation of sulfite to sulfate in wine was estimated from the ITP–ZE quantitation of sulfate performed at different times after the addition of hydrogen peroxide to the formaldehyde stabilized sample. Model and wine samples were taken for this estimation to assess a potential influence of wine matrices on the rate of oxidation. We found that the oxidation was finished within 15 min (no increase of the sulfate peak area was detected when the reaction time was prolonged to 30 min). Very good repeatabilities of the peroxide oxidation of sulfite illustrate the data obtained from the reactions performed in parallel on aliquot parts of the formaldehyde stabilized wine samples (Table 4).

Table 3
Parameters of the regression equations and correlation coefficients for the calibration graphs of sulfate

Intercept (mV s)	Slope (mV s l/mg)	Correlation coefficient	n[a]	Concentration range[b] (mg/l)
Sulfate				
0.31	17.88	0.9994	15	0.6–7.2
Sulfate formed by oxidation of sulfite[c]				
0.97	17.14	0.9996	15	0.6–7.2

[a] n: number of data points.
[b] The concentration range corresponds to 0.5–6 mg/l concentrations of sulfite.
[c] Sulfite bound in HMS was oxidized.

Wine contains sulfate (see an electropherogram in Fig. 3b) and, therefore, the results obtained for the oxidized sample had to be corrected accordingly. This required the determination of sulfate in the sample (preferably with free sulfite bound in HMS) before and after the peroxide oxidation. The data presented in Table 5 for two of the wine samples taken into a detail study were obtained by such a quantitation procedure.

Quantitations of total sulfite in wine based on the external calibration and standard addition (sulfite added as HMS) show very good agreements (Table 5). Complemented by the recovery data (Table 5), they indicate that the hydrogen peroxide oxidation with the ITP–ZE determination of sulfate is accurate as far as the determination of total sulfite in wine is concerned. Such a statement supports also the results of analyses performed with the same samples in which a distillation isolation of total sulfite from wine (see Section 2) preceded the determination of sulfate (Table 5).

Concentration limit of detection (cLOD) for sulfite in wine, set by the ITP–ZE procedure on the CC chip, was estimated in the way as recommended for elution chromatography [31]. Here, the sulfate peak heights, obtained from the responses of the conductivity detector in the ZE stage of the combination, provided the input data used in the cLOD estimation. This procedure gave the cLOD value of 90 μg/l of sulfite for a 0.9 μl load of the sample on the chip. Such a detectability made possible the determination of total sulfite when this was present in wine at a 15 mg/l concentration (the sample dilution is included).

The ITP–ZE separations were performed with a hydrodynamically closed separation compartment of the chip and with suppressed electroosmotic flow of the solution in which the separation is performed (see Section 2). Such transport conditions, minimizing within run and run-to-run fluctuations of the migration velocities of the separated constituents on the chips [24], undoubtedly, contributed to highly reproducible separations as achieved in this work (see the data in Tables 2 and 4).

Table 4
Reproducibilities of the migration times and peak areas of sulfate formed by a hydrogen peroxide oxidation of total sulfite in wine samples

Wine sample	ITP pretreatment time (s)[a]		Migration time in ZE stage (s)[b]		Peak area (mV s)		n[c]
	Mean	S.D.	Mean	S.D.	Mean	S.D.	
Heppenheimer Centgericht Spätburgunder (50-fold diluted)	262	0.3	338	0.2	19.6	0.3	3
Műller Thurgau (50-fold diluted)	259	0.5	343	0.7	35.5	0.5	3

The separations were carried out in the electrolyte system given in Table 1. The driving current was stabilized at 30 μA in both channels. For wine specifications and the sample preparation procedures, see Section 2.

[a] A time of entrance of the sulfate zone to the bifurcation section of the CC chip (BF in Fig. 2).

[b] A migration time of sulfate in the ZE stage.

[c] n: number of parallel oxidations on aliquots of the same sample formaldehyde stabilized sample.

Table 5
Determination of total sulfite in wine samples using two different sample clean up methods

Wine sample	Sample clean up	Dilution (fold)	Determined[a] (mg/l)	S.D. (mg/l)	Recovery (%)
Heppenheimer Centgericht Spätburgunder	ITP-CZE	50	45.3[b]	0.6	–
	ITP-CZE	50	45.0[c]	–	99
	Distillation 1	20	47.8[b]	1.2	–
	Distillation 2	50	45.0[b]	1.3	–
Műller Thurgau	ITP-CZE	50	84.0[b]	1.3	–
	ITP-CZE	50	84.9[c]	–	101
	Distillation 1	40	86.5[b]	2.5	–
	Distillation 2	20	87.2[b]	0.4	–

For specifications of wine samples and the sample preparation, see Section 2.

[a] Mean values obtained from three parallel ITP–ZE determinations.

[b] A content of total sulfite determined from the calibration graph.

[c] A content of total sulfite determined by the standard addition method.

4. Conclusions

This work showed that ITP–ZE on the CC chip with conductivity detection provides simple and, at the same time, rapid (ca. 10 min lasting separation) and highly selective method to the determination of sulfate formed by an in-sample oxidation of total sulfite in wine by hydrogen peroxide at pH ≈10. Electropherograms (Figs. 3 and 4) clearly document that the sample clean up, linked with the use of the ITP–ZE separation, eliminated the anionic matrix constituents in an extent comparable to a distillation isolation of sulfite.

Although not essential [14], we favored a formaldehyde stabilization of free sulfite in wine to eliminate an uncontrolled oxidation of this sulfite form. Such a precaution was taken to achieve an unbiased determination of sulfate present in the original wine sample (this determination was needed to obtain the sulfate concentration equivalent to the concentration of total sulfite in the sample).

Both ITP and ZE, performing specific analytical tasks in the ITP–ZE separation on CC chip, contributed to a 90 μg/l cLOD value for sulfite when the oxidized sample was loaded by a 0.9 μl sample injection channel of the chip. Such a detection performance allowed the quantitation of total sulfite when its concentration in wine was 15 mg/l. We should note that this value is not a minimum attainable by ITP–ZE on the present CC chip because a maximum sample load for wine (the volume of wine loaded onto the chip that still provides a full recovery of sulfate in the ITP stage of the run) was not reached in our experiments.

The ITP–ZE separations were carried out in a hydrodynamically closed separation compartment of the chip with suppressed electroosmotic flow. It can be stated [24] that such transport conditions contributed to high precisions of both the migration and quantitation data as attained for sulfate in this work (Tables 2 and 4).

Recoveries of sulfite as determined for two wine samples (Table 5) indicate a very good accuracy of the present method. Such a conclusion also supports agreements of the quantitation of total sulfite as obtained for different sample preparations (Table 5).

It seems reasonable to assume that the use of the present method can be extended to the determination of total sulfite in other food products. In addition, considering the results of our previous work [17], it is logical to state that ITP–ZE on the CC chip, combined with simple pre-column sample preparation procedures, offers a flexible analytical tool to the determination of various sulfite forms in food products.

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