

Short communication

# Determination of sulphite and sulphate by ion chromatography using a weakly basic phthalate eluent

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## Abstract

A simple ion chromatographic method was developed for the determination of sulphite and sulphate using an ODS column dynamically coated with cetylpyridinium bromide and 0.5 mmol l<sup>-1</sup> phthalate–0.01% triethanolamine–5% methanol at pH 8.5 as eluent. Many inorganic and organic anions had little effect on the determination. The analytical results for sulphite in wine obtained by the proposed method agreed with those obtained by the iodimetric method.

*Keywords:* Wine; Sulfito; Sulfate; Inorganic anions

## 1. Introduction

Sulphite is an interesting anion, but its determination is very difficult, because most of it is oxidized to sulphate in aqueous solution within 1 day. Some ion chromatographic procedures [1–9] have been reported for the determination of sulphite. The use of formaldehyde as a sulphite stabilizer [1,3,6,8,9] was restricted in a strongly basic eluent, because hydroxymethanesulphonate, the reduction product of sulphite and formaldehyde, decomposes to sulphite in a strongly basic solution. A strongly basic eluent also gave poor pH maintenance. We had already studied sulphite stabilizers by ion chromatog-

raphy and proposed methanol as a suitable sulphite stabilizer [10]. Methanol did not affect the chromatogram of sulphite and protected it against air oxidation in the absence of metals for at least 48 h.

Sulphite in wine had been often determined by the distillation–alkali titration method [11], but this involves a troublesome procedure. Flow injection analysis has recently been proposed for the determination of sulphite in wine [12], but ion chromatography has not been reported. This paper describes a simple and rapid method for the determination of sulphite and sulphate in wine by ion chromatography with indirect UV detection using an ODS column coated with cetylpyridinium bromide and 0.5 mmol l<sup>-1</sup> phthalate–0.01% triethanolamine–5% methanol at pH 8.5 as eluent.

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## 2. Experimental

The ion chromatographic equipment consisted of a pump (CCPD; Tosoh, Tokyo, Japan), a variable-wavelength UV-Vis detector (UV-8000; Tosoh) monitoring at 265 nm, an injector (Rheodyne, Cotati, CA, USA) with a 100- $\mu$ l sample loop, a column oven (CO-8000; Tosoh) maintained at 35°C and a flat-bed pen recorder (YEW Type 3066; Yokogawa, Tokyo, Japan). All chemicals were of analytical-reagent grade and deionized, distilled water, further filtered through a 0.45- $\mu$ m membrane filter, was used throughout. Standard sulphite solution in 5% (v/v) methanol was prepared daily from sodium sulphite. Standard sulphate solution was prepared from sodium sulphate. The other anion solutions were also prepared from the corresponding sodium salts.

The eluent was 0.5 mmol l<sup>-1</sup> phthalate–0.01% triethanolamine–5% methanol, adjusted to pH 8.5 with dilute sodium hydroxide solution. The eluent was degassed ultrasonically before use.

Separation columns were prepared from 50  $\times$  4.6 mm I.D. columns packed with ODS resin (Capcell Pak C18, AG120, particle size 5  $\mu$ m; Shiseido, Tokyo, Japan) and then dynamically coated with cetylpyridinium bromide (CPyBr). The coating procedure was similar to that used in previous work [13]. The ion-exchange capacity of the coated column was about 0.15 mequiv. per column. Regeneration of the column was carried out by washing with methanol and then coating again with CPyBr.

A cask wine sample taken after pulling out a bung was immediately passed through a cation-exchange resin (Amberlite, AG IR-120B, H<sup>+</sup> form) column (30.0  $\times$  1.5 cm I.D., resin bed 15.0 cm). The effluent was collected in a 10-ml flask to which 1 ml of methanol had been added, resulting in a 10% methanol solution. A further fifteen-fold diluted solution of the sample was passed through an ODS pre-filter (Toyopak ODS, size M; Tosoh) and injected on to the column. The concentrations of sulphate and sulphite were calculated from calibration graphs that were constructed daily from the concentration and the peak area of sulphite (retention

time 8.4 min) and sulphate (11.6 min) on the chromatogram.

Sulphite in wine was also determined by the following iodimetric procedure [14]. An aliquot of a wine sample was placed in an erlenmeyer flask, 20 ml of 0.01 mequiv. l<sup>-1</sup> iodide solution and 10 ml of acetate buffer solution (pH 3.9) were added and the mixture was titrated with 0.01 mequiv. l<sup>-1</sup> standard thiosulphate solution. The concentration of sulphite in wine was then calculated.

## 3. Results and discussion

Sulphite ion was present almost entirely as hydrogensulphite at pH < 8. Although maintenance of the pH of the phthalate eluent above 7 was very difficult, the addition of triethanolamine to the phthalate eluent gave satisfactory pH maintenance at pH > 7 and had little effect on the chromatograms of sulphite and sulphate. The effect of eluent pH on the retention times of anions was examined in the pH range 7.5–9.25 and the results obtained are shown in Fig. 1. The

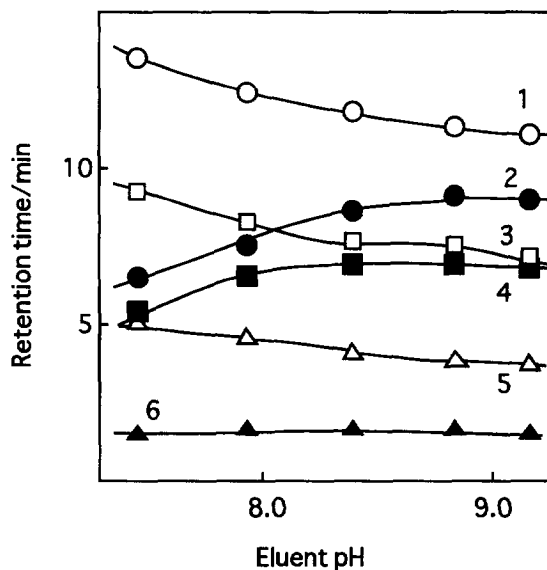


Fig. 1. Effect of eluent pH on the retention times of anions. Eluent, 0.5 mmol l<sup>-1</sup> phthalate–0.01% triethanolamine; flow-rate, 1.0 ml min<sup>-1</sup>. 1 = Sulphate; 2 = sulphite; 3 = nitrate; 4 = hydrogenphosphate; 5 = bromide; 6 = chloride.

retention times of sulphate, bromide, chloride and nitrate decreased slightly with increasing eluent pH, but those of hydrogenphosphate and sulphite increased with increasing pH up to 9.0 and decreased slightly above pH 9.0. Phosphate and sulphite were converting into hydrogenphosphate and sulphite from dihydrogenphosphate and hydrogensulphite in the pH range 7.0–9.0, respectively. Broad peaks of sulphite and hydrogenphosphate were obtained at pH < 8.5. An eluent pH of 8.5 was adopted, showing good resolution and sharp peaks of the anions. An eluent phthalate concentration of  $0.5 \text{ mmol l}^{-1}$  was chosen in order to achieve a good separation of the anions.

The effect of the triethanolamine concentration was examined. The chromatogram of nitrate, sulphite and sulphate obtained with an eluent containing 0.01% triethanolamine is shown in Fig. 2. Irregular chromatograms with a peak just in front of that of each anion were obtained with increasing concentration of triethanolamine. An eluent with more than 0.01% triethanolamine added gave a satisfactory buffer effect.

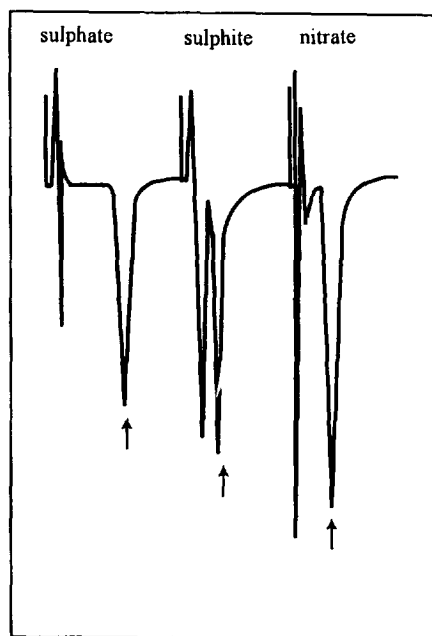


Fig. 2. Effect of triethanolamine concentration on the chromatograms of sulphite, sulphate and nitrate. Eluent,  $0.5 \text{ mmol l}^{-1}$  phthalate–0.01% triethanolamine (pH 6.8).

Table 1

Effect of methanol concentration (0–10%) on the retention times of anions

Anion	Retention time (min)		
	0%	5%	10%
Iodide	29.8	18.4	12.8
Nitrate	7.7	5.0	4.8
Oxalate	13.5	12.1	12.6
Hydrogenphosphate	7.0	7.0	7.0
Sulphate	11.6	11.6	11.6
Sulphite	8.4	8.4	8.4
Tartrate	12.1	10.7	10.9
Thiocyanate	>40	>40	31.5
Thiosulphate	37.0	32.6	29.5

Baseline separation of sulphite and nitrate was established by the addition of methanol to a  $0.5 \text{ mmol l}^{-1}$  phthalate–0.01% triethanolamine–5% methanol eluent. This was explained by the decreased hydrophobic interaction. As shown in Table 1, the retention times of more hydrophobic anions such as nitrate decreased with increasing methanol concentration and those of the other anions such as sulphite and sulphate were almost constant. Hence the resolution of sulphite and nitrate was improved.

The eluent  $0.5 \text{ mmol l}^{-1}$  phthalate–0.01% triethanolamine–5% methanol was recommended. The calibration graphs were rectilinear for  $0.02$ – $400 \mu\text{g ml}^{-1}$  of sulphite (correlation coefficient  $r = 0.9830$ ) and  $0.04$ – $350 \mu\text{g ml}^{-1}$  of sulphate ( $r = 0.9906$ ). The determination limit for sulphite was about one order of magnitude lower than that ( $5 \cdot 10^{-6} \text{ mol l}^{-1}$ ;  $0.4 \mu\text{g l}^{-1}$ ) reported using flow injection analysis [12]. The relative standard deviations (R.S.D.s) ( $n = 5$ ) were 1.2% and 1.7% for a  $10 \mu\text{g ml}^{-1}$  concentration of sulphite and sulphate, respectively.

The retention times of various inorganic and organic anions were determined and are reported in Table 2. Organic anions, such as acetate, lactate, malate and citrate, are often present in wine samples. Acetate and lactate were eluted at shorter retention times and citrate was strongly retained. Hence no interference was encountered in the determination of sulphite and sulphate. A

Table 2  
Retention times of various anions

Anion	Retention time (min)	Anion	Retention time (min)
Acetate	<2.0	Iodate	<2.0
Benzoate	ND <sup>a</sup>	Iodide	18.4
Bromate	<2.0	Lactate	<2.0
Bromide	3.9	Malate	9.5
Chlorate	9.5	Nitrate	5.0
Chloride	<2.0	Nitrite	<2.0
Citrate	>40	Oxalate	12.1
Fluoride	<2.0	Sulphate	11.6
Formate	<2.0	Sulphide	<2.0
Gluconate	<2.0	Sulphite	8.4
Glutamate	<2.0	Tartrate	10.7
Hydrogencarbonate	<2.0	Thiocyanate	>40
Hydrogenphosphate	7.0	Thiosulphate	32.6

<sup>a</sup> Not detected.

typical chromatogram of a wine sample is shown in Fig. 3. The peak that appeared between sulphite and sulphate was confirmed to be due to nitrate. The other peaks were not identified.

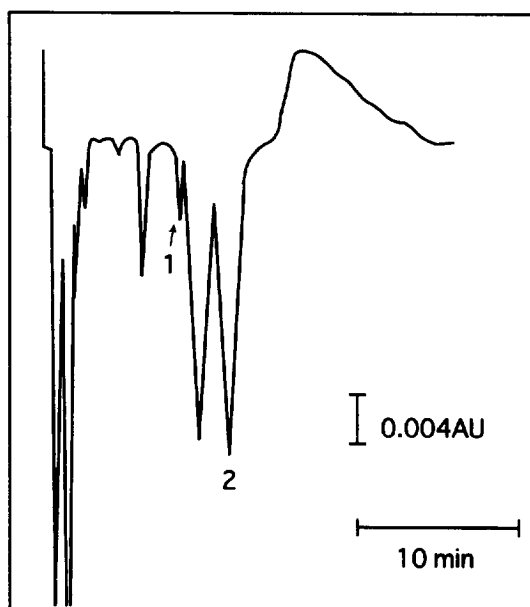


Fig. 3. Chromatogram of a wine sample. Eluent, 0.5 mmol l<sup>-1</sup> phthalate–0.01% triethanolamine–5% methanol (pH 8.5). Peaks: 1 = sulphite; 2 = sulphate.

peak that appeared in front of sulphite was confirmed to be due to nitrate. The other peaks were not identified.

Sulphite and sulphate were determined in five red wine samples by the proposed method. The results obtained and the results for sulphite determined by the iodimetric method [14] are shown in Table 3. The concentrations of sulphite determined by the proposed ion chromatographic method agreed well with those obtained by the iodimetric method. The concentrations of sulphite were of the same order as those reported using flow injection analysis [12].

Table 3  
Analytical results for wine samples

Sample No.	Sulphite concentration (μg ml <sup>-1</sup> )		Sulphate concentration (μg ml <sup>-1</sup> )
	Proposed method	Iodimetric method	
1	529.5	523.0	2584.9
2	129.6	123.2	2802.8
3	182.4	180.4	1495.6
4	174.8	173.2	1802.6
5	307.0	310.3	2368.3

#### 4. Conclusions

The proposed simple ion chromatographic method is suitable for the determination of sulphite and sulphate using 0.5 mmol l<sup>-1</sup> phthalate–0.01% triethanolamine–5% methanol as eluent at pH 8.5. Sulphite was determined in wine samples without a tedious pretreatment such as distillation.

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