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The determination of the sulphite content of some foods and beverages by capillary electrophoresis

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A method for the determination of the sulphite content in foods and beverages by capillary electrophoresis (CE) is described. The sulphite is converted to sulphur dioxide and finally to sulphate using a Monier–Williams distillation. The sulphate is then determined by CE using a 75 μm fused silica capillary column with a buffer consisting of 5 mM sodium chromate and 0.5 mM OFM Anion–BT reagent, pH 8.0, with indirect UV detection at 254 nm. Nitrate was used as the internal standard. The levels of sulphite in the products are in good agreement with those determined by titrimetry, except for one sample of fresh prawns, fresh garlic and some processed foods containing garlic and onion, where the levels determined by CE are lower. The instrument repeatability of the CE procedure is satisfactory and the level of detection is 5 mg/kg.

INTRODUCTION

Sulphites are added as preservatives to a wide variety of foods and beverages available in Australia (Anon., 1994). The Monier–Williams procedure is the most common analytical procedure for quantifying sulphite in foods and beverages (Williams, 1984*a*). The sulphite is converted into sulphur dioxide with either hydrochloric acid or orthophosphoric acid, and the sulphur dioxide distilled into 3% peroxide solution where it is oxidized to sulphuric acid. The sulphuric acid is then titrated with standardized sodium hydroxide. However, this procedure is not applicable to dried onions, leeks or cabbage. A colorimetric procedure based on the addition of sodium tetrachloromercuriate, pararosaniline and formaldehyde to an aqueous extract of the food is also used to determine the sulphite content of dried fruit (Williams, 1984*b*). Ion chromatography with conductivity and electrochemical detection has also been used in conjunction with acid distillation for sulphite determination in food (Sullivan & Smith, 1985; Anderson *et al.*, 1986). Recently, high-performance ion chromatography (HPIC) with conductivity detection was used to determine the sulphite content in foods (Ruiz *et al.*, 1994). The sulphite was converted to sulphur dioxide with acid, distilled from the sample and trapped in dilute sodium hydroxide, where it was oxidized to sulphate with 0.3% peroxide solution. The sulphate was then determined by HPIC. Other determinative methods of analysis used in conjunction with the Monier–Williams distillation include coulometry and polarography and these are detailed in an extensive review by Fazio & Warner (1990).

Analytical methods based on capillary electrophoresis (CE) as the determinative step are rapidly gaining acceptance as robust analytical procedures (Trenerry *et al.*, 1994*a*,*b*; Pant & Trenerry, 1995; Thompson & Trenerry, 1995). CE procedures are often faster and more cost-effective than other instrumental techniques and have the added advantage that most determinations can be carried out using the same fused silica capillary (Thompson *et al.*, 1995*a*,*b*). CE has been used very successfully to determine a number of different anions in a variety of samples (Romano *et al.*, 1991). Up to 30 different anions have been separated in less than 5 min using an uncoated fused silica capillary column and a buffer consisting of 5 mM sodium chromate and 0.5 mM OFM Anion–BT reagent (Jones & Jandik, 1991). The anions are detected with indirect UV detection at 254 nm. Sulphate is well separated from a number of other commonly occurring anions (e.g. chloride, nitrate) and can be detected at very low levels. This paper describes a rapid and sensitive CE method for the determination of sulphite (as sulphate) in a variety of foods and beverages using a Monier–Williams distillation to liberate sulphur dioxide, subsequent oxidation of sulphur dioxide to sulphuric acid followed by the determination of sulphate by CE. The CE method monitors the sulphate levels free from other volatile compounds that might interfere with the acid–base titration. The results are compared with those obtained with the traditional

Monier–Williams method that is used in the author's laboratory.

MATERIALS AND METHODS

Materials

Potassium chloride and potassium sulphate were obtained from BDH Chemicals, Pty Ltd (Kilsyth, Australia). Sodium sulphite was obtained from Ajax Chemicals (Sydney, Australia), and potassium nitrate was obtained from May and Baker Australia Pty Ltd (Victoria, Australia). Sodium chromate was obtained from Mallinckrodt Inc. (Kentucky, USA) and OFM Anion–BT reagent was obtained from Waters (Massachusetts, USA). All other chemicals were of AR grade and used without further purification.

Samples

The samples were products available for purchase within Australia. The fresh produce was analysed as soon as practical after purchase, and the packaged foods and beverages were analysed before the 'used-by' dates.

Preparation of standards, samples and buffers

Standards

CE Stock solutions of sulphate, chloride and nitrate were prepared at a concentration of 1000 μg/ml in deionized water. Working standards of different concentrations were prepared in 1.5% hydrogen peroxide solution. Nitrate was used as the internal standard at a concentration of 25 μg/ml. The solutions were filtered through a 0.8 μm cellulose acetate filter unit prior to analysis.

Samples

CE and Monier–Williams titration. The solid samples were blended with a commercial food processor until homogenous, and the liquids were mixed thoroughly before a suitable aliquot of the sample (20 g for solids and 20 ml for liquids) was taken. Fifty millilitres of deionized water were added to the sample and the mixture subjected to the standard Monier–Williams distillation, using 5 ml of a 1:2 mixture of concentrated hydrochloric acid and water to convert sulphite to sulphur dioxide. The sulphur dioxide was distilled into 25 ml 3% hydrogen peroxide solution. This solution was quantitatively transferred with deionized water to a 50 ml volumetric flask containing the internal standard (nitrate) at a final concentration of 25 μg/ml. If the samples contained high levels of sulphite, the peroxide solution was diluted accordingly before the addition of the internal standard. A small aliquot of the solution (2 ml) was filtered through a 0.8 μm cellulose acetate filter before CE analysis. The remainder of the solution was then titrated with standardized sodium hydroxide as prescribed by the Monier–Williams procedure.

Buffer for CE

Five millilitres of OFM Anion–BT reagent was diluted to 200 ml with 5 mM sodium chromate solution (Romano *et al.*, 1991). The buffer was prepared as required and filtered through a 0.45 μm cellulose acetate filter unit prior to use. The buffer solutions were changed daily.

Apparatus

CE

The analyses were performed with a 75 cm × 75 μm i.d. fused silica capillary (Polymicro Technologies, Arizona, USA) with an effective length of 50 cm to the detector. An Isco Model 3140 Electropherograph (Isco Inc., Lincoln, Nebraska, USA) operating at −15 kV and at 28°C was used for the analyses. The sample was loaded onto the column under vacuum (vacuum level 2, 10 kPa·s). The capillary was flushed with running buffer for 2 min between analyses. The compounds were detected at 254 nm at 0.005 AUFS in the indirect operating mode. Electropherograms were recorded with either the ICE Data Management and Control Software supplied with the Model 3140 Electropherograph or a HP 3350 Laboratory Data System (Hewlett-Packard, Palo, Alto, California, USA). Peak areas were used in the calculations.

RESULTS AND DISCUSSION

The separation of sulphate and nitrate anions using the conditions described in the Materials and Methods section is well documented in the literature (Romano *et al.*, 1991; Jones & Jandik, 1991). To achieve the separation of the anions, a cationic surfactant (OFM Anion–BT reagent) is added to the UV absorbing electrolyte (chromate) causing the electro-osmotic flow to move towards the anode, forcing the anions to migrate in the same direction as the electro-osmotic flow from the injection end to the detector end of the instrument.

The CE procedure was first validated with standard solutions of different concentrations to determine the linearity range and to check the repeatability of the technique. The standard solutions were run seven times to obtain instrument repeatability data. For the quantitative analyses, a variety of market samples were analysed for sulphite content. A number of sample solutions were analysed seven times by CE to obtain instrument repeatability data. The levels of sulphite determined by CE were compared with the levels determined on the same solutions by titrimetry. Peak areas were used in the calculations. The areas were not corrected for changes in migration times as the area of the internal standard was used in the calculations.

The detector response for sulphate was shown to be linear to 50 μg/ml at 0.005 AUFS and the instrument repeatability data for area calculation (%CV) for all of the solutions were satisfactory (standard concentration = 1 μg/ml, %CV = 8.5; standard concentration = 2 μg/

Table 1. Comparison of the levels of sulphite (expressed as sulphur dioxide) determined by CE and titimetry for a variety of foods and beverages

Sample	CE	Titimetry
	Sulphur dioxide (mg/litre)	
Cordial		
Brand 1	135	120
Brand 2	100	90
Brand 3	95	90
Brand 4	75	65
Wine		
Brand 1	95	95
Brand 2	85	85
	Sulphur dioxide (mg/kg)	
Fresh vegetables		
Asparagus	< 5	20
Cabbage	< 5	< 5
Chives	< 5	< 5
Onions	< 5	< 5
Spring onions	< 5	< 5
Garlic	20	30
Garlic[a]	20	20
Processed foods		
Dried apricot	2460	2470
Sour mustard	2340	2200
Mustard pickle	300	290
Onion slices	30	55
Garlic flakes	10	50
Seasoning powder	< 5	40
Soy sauce	< 5	10
Chilli garlic sauce	< 5	65
Seafood		
Seafood sticks	< 5	< 5
Prawns 1	5	20
Prawns 2	< 5	5
Prawns 2[a]	< 5	< 5
Mussels	< 5	< 5
Abalone	< 5	< 5

[a]Phosphoric acid used instead of hydrochloric acid in the distillation.

ml, %CV = 8.0; standard concentration = 5 μg/ml, %CV = 3.7; standard concentration = 10 μg/ml, %CV = 1.8; standard concentration = 20 μg/ml, %CV = 2.1; standard concentration = 50 μg/ml, %CV = 1.4). The presence of 1.5% hydrogen peroxide in the solutions did not affect the separations, and the migration times of sulphate and nitrate anions were very consistent over repeated analyses.

The sulphite content of a number of samples was then determined by CE and compared with the levels determined by titrimetry. The level of sulphite (determined as sulphur dioxide) for the samples containing added sulphite were in excellent agreement and are displayed in Table 1. This was also the case for the majority of the fresh produce and seafood. However, lower levels were obtained by CE for fresh garlic, onion slices and other processed foods containing onion or garlic. Electropherograms for apricots and mustard pickle are shown in Fig. 1. Four samples with different levels of added sulphite were analysed seven times to determine the instrument repeatability data (mustard pickle SO_2, 300 mg/kg, %CV = 2.2; cordial SO_2, 100 mg/kg, %CV = 0.9; onion slices SO_2, 30 mg/kg, %CV = 2.8; garlic flakes SO_2, 10 mg/kg, %CV = 5.6). The CE procedure has a level of reporting of 5 mg/kg for a 20 g sample aliquot. This equates to a 50 ml distillate containing sulphate at a concentration of 2 μg/ml which corresponds to the lowest standard used in the calculations. Lower levels of reporting could be achieved by using a larger sample aliquot and a smaller distillate volume, however, this was not possible with the available apparatus.

A peak corresponding to chloride was present in varying amounts in most of the samples. The chloride peak was larger in the fresh garlic, onion slices and fresh prawns. Only a small portion of the chloride peak in the electropherograms could be attributed to carryover of HCl gas during the distillation as the electropherogram of the reagent blank showed only small amounts of chloride (Fig. 2). This suggests that the chloride was produced from naturally occurring compounds in the samples during the distillation and is then oxidized to hydrochloric acid by the 3% hydrogen peroxide solution. This would then give rise to a higher value for sulphur dioxide, as the sulphur dioxide content is proportional to the amount of hydrogen ions present in the hydrogen peroxide solution. The chloride content of the peroxide solutions from fresh garlic and fresh prawns diminished when orthophosphoric acid was used instead of hydrochloric acid in the distillation (Fig. 3). The amount of chloride present in the reagent blank was also small. Lower levels of sulphite (determined as sulphur dioxide by titimetry) were also obtained for these foods when orthophosphoric acid was used as the digesting acid (see Table 1). A corresponding decrease in the amount of chloride was seen in the electropherograms of these samples. The CE procedure measures sulphate ion concentration, and so is a more accurate representation of the amount of sulphur dioxide released during the distillation. The level of sulphate (and therefore sulphur dioxide) in the hydrogen peroxide solutions for garlic and prawns was the same whether hydrochloric acid or orthophosphoric acid was used (Table 1).

The Monier–Williams procedure is applicable in the presence of volatile sulphur compounds (Williams, 1984*a*). However, the sulphate ion concentration in the hydrogen peroxide solution could be enhanced by the presence of volatile organosulphur compounds in the foods which are distilled into the 3% hydrogen peroxide solution and oxidized to sulphate. This might explain the levels of sulphite present in the one sample of prawns, garlic and processed foods.

All of the data were collected on the hydrogen peroxide solutions from the Monier–Williams distillation before titration. The peroxide solution from the fresh garlic was analysed by CE after titration. The electropherogram was identical to the one previously recorded for the solution before titration and so could therefore be used for the determinations.

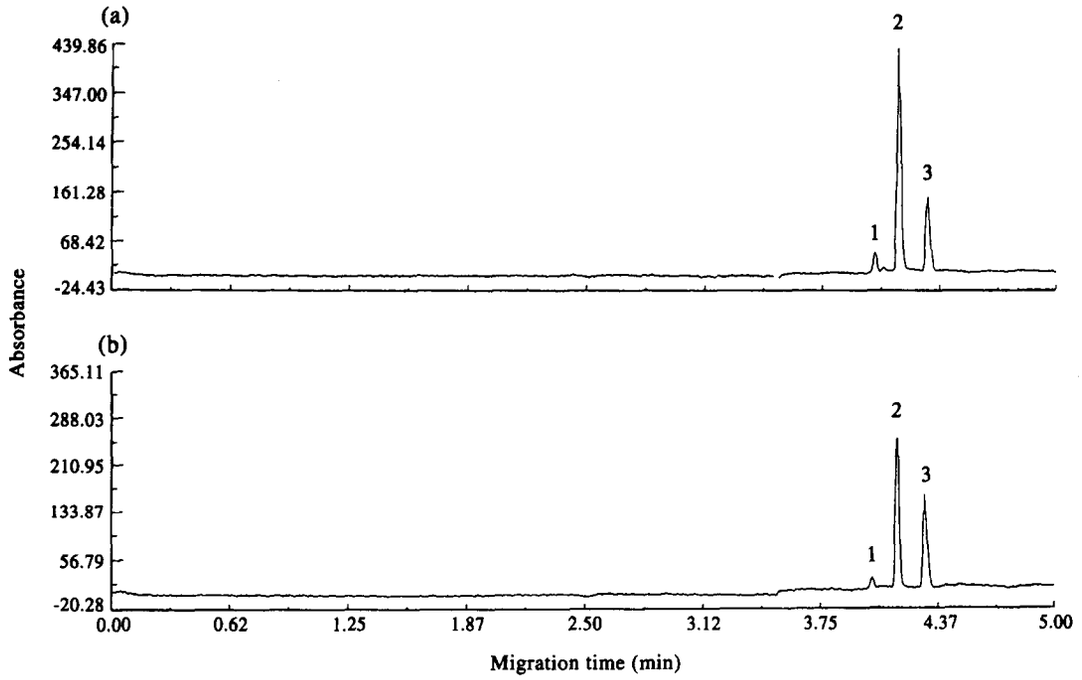

Fig. 1. Electropherograms of (a) mustard pickle and (b) dried apricots showing (1) chloride, (2) sulphate and (3) nitrate using a 75 μm fused silica capillary column with a buffer consisting of 0.5 mM Anion–BT reagent and 5 mM sodium chromate, pH 8.0.

CONCLUSION

The CE procedure outlined was found suitable for quantifying the sulphite content of a variety of food and beverages, including samples that are not usually analysed by the traditional Monier–Williams technique. The limit of detection (5 mg/kg) is the same as the Monier–Williams method. The instrument repeatability data (%CV) was satisfactory for standard and sample solutions, and there was no evidence of any

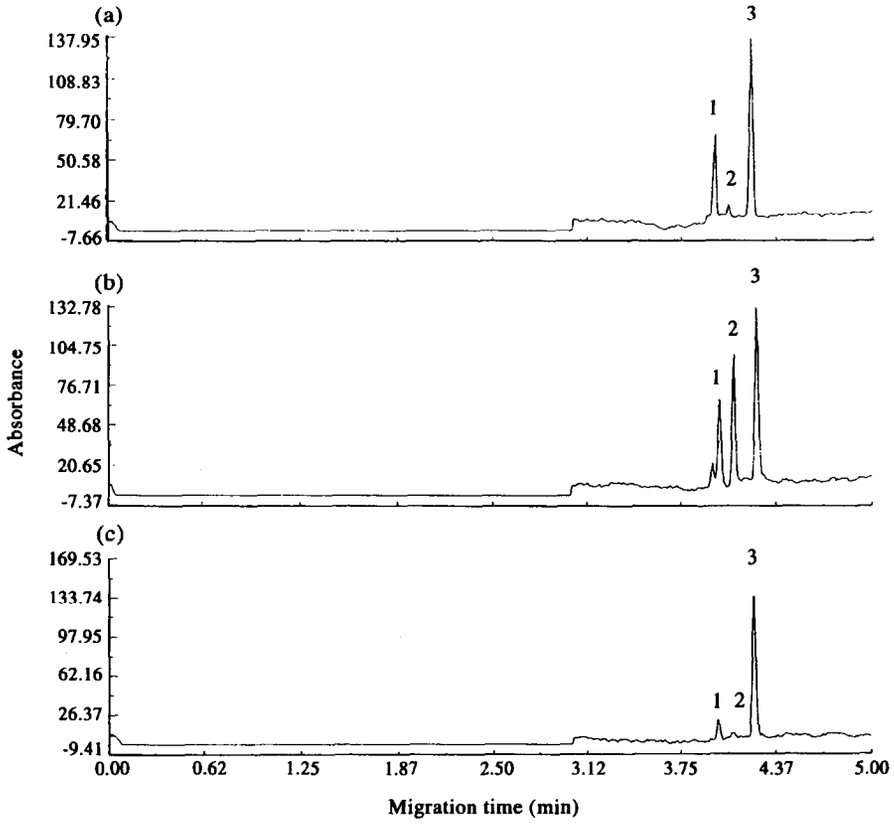

Fig. 2. Electropherograms of (a) fresh prawns, (b) fresh garlic and (c) reagent blank showing (1) chloride, (2) sulphate and (3) nitrate with hydrochloric acid used as the digesting acid.

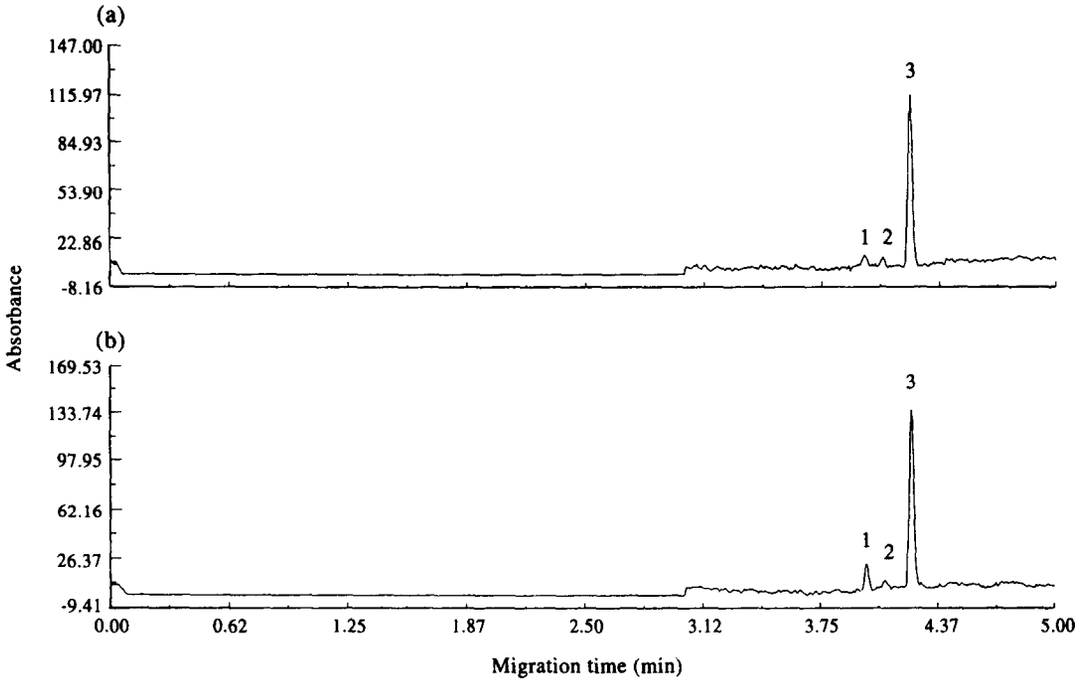

Fig. 3. Electropherograms of (a) fresh prawns and (b) reagent blank showing (1) chloride, (2) sulphate and (3) nitrate with orthophosphoric acid used as the digesting acid.

interfering compounds that would affect the CE determination.

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