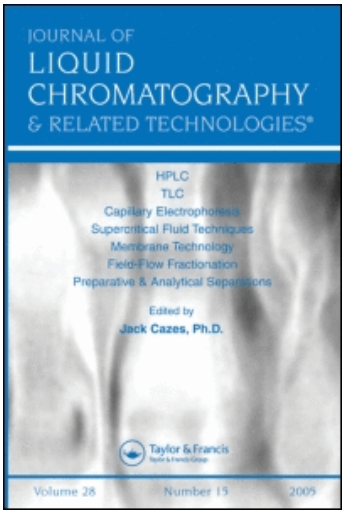

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HIGH PERFORMANCE ION CHROMATOGRAPHY DETERMINATION OF TOTAL SULFITES IN FOODSTUFFS

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ABSTRACT

An alternative chromatographic method based upon a combination of a modified Monnier-Williams procedure and an Ion Chromatography separation and quantitation of sulfite, have been developed. The collected gaseous SO_2 is oxidized to sulfate with hydrogen peroxide. IC determination was carried out with an anion-exchange polymetacrylate column, borate/gluconate as eluent and conductivity detection. The combined method shows a good detection limit as well as a high chromatographic resolution. It is also applicable to the analysis of several foodstuffs.

INTRODUCTION

Sulfites in various forms have been added to foods for centuries. Only recently has the widespread use of sulfites in foods become an issue of health concern. Certain individuals have been found to exhibit adverse reactions (mainly asthmia) to sulfite residues in foods (1,2).

The AOAC Monnier-Williams method (3) for sulfite analysis has been the method of choice for many years, although its application has several drawbacks that have been recognised and cited in the literature (4,5).

A number of alternative methods has been developed. Ion chromatographic techniques have been reported for sulfite analysis involving, in some cases, a process of previous distillation (6,7,8) whereas in others distillation is replaced for extraction (9,10,11,12). Those techniques permit a rapid, precise and reliable sulfites determination.

In view of the fact that amongst the existing difficulties in analytical sulfite ion measurement are volatility and inestability to air oxidation, which could be overcome by the indirect detection of stable sulfate of the distilled gaseous SO_2, IC techniques can monitor the sulfite levels free of interferences from other volatile anions often present in foods as well as from the reagents employed during the extraction and oxidation of sulfite (13).

Once the above-mentioned chromatographic procedures were evaluated, we chose as working method an anion-exchange with conductivity detection and borate/gluconate as eluent to determinate sulfites by the indirect detection of sulfates.

MATERIAL AND METHOD

Reagents

All the reagents used were of analytic grade; organic solvents of high purity grade for HPLC; water was Milli-Q (Millipore Corp. Bedford M.A. 01730, U.S.A.) deionized. Standard reagents of sodium sulfite and sulfate were purchased from Merck (D-6100 Darmstadt, Germany).

Equipment

Ion-Chromatographic system (Millipore-Waters, Milford M.A, U.S.A.) ILC-1 composed of a manual injector with a 100 ul loop,

conductivity detector (430), Programmable Solvent Delivery module (590); Data Module Integrator (745) and anionic column IC-PAK™.

Distilling Unit: Kjeltec System 1026 (Tecator AB, S-26301 Höganäs, Sweden).

Samples

Analyzed samples were purchased from food stores after a sampling carrier out by The Food Health Department in different Regional Communities.

Method

EXTRACTION: Samples were extracted by acid distillation according to a modification of the original Monnier-Williams method developed in our laboratory (14).

The sample was first minced in a homogenizer (a domestic blender). Approximately 20 g of the homogenate was distilled for 10 minutes in 70 ml water containing 3 ml HCl 37%. The liberated sulfite was trapped in a solution of 0.5 ml 1N sodium hydroxide plus 4.5 ml water, and oxidized to sulfate with of about 0.3% hydrogen peroxide.

Purification was carried out by filtering 2-3 ml of extract through an 0.45 μm membrane filter (MIllex HV, Millipore). This solution was applied to a Sep-Pak C_{18} cartridge (Millipore-Waters) which was pretreated with 5 ml of methanol and 5 ml of water. Eluates aliquots of 100 μl were injected into the chromatograph.

IC DETERMINATION: High Performance Ion Chromatography was carried out under the following conditions: conductivity detection; eluent sodium borate/gluconate pH 8.5 (300 μS Conductivity); flow rate, 1 ml/min.

Linearity and sensitivity of the detector were calculated from a series of standard solutions from 1 to 100 μg/ml, prepared from sodium sulfite oxidized to sulfate with 0.3% hydrogen peroxide.

RESULTS AND DISCUSSION

As the determination of sulfite is quite difficult due to rapid oxidation of sulfite to sulfate by dissolved oxygen, and as IC with conductivity detection gives one of the most accurate and precise values for sulfate, we decided to choose this technique as working method.

The first step was to check out that oxidation of sulfite to sulfate with hydrogen peroxide was quantitative. For this purpose standard solutions with an equal concentration of sodium sulfate and oxidized sodium sulfite (with 0.3% hydrogen peroxide) were prepared. It was observed chromatographic peaks of both anions and their RT coincided, and, concentration being equal, the areas were similar.

Figure 1 shows the chromatogram for sodium sulfate and sodium sulfite oxidized under the chromatographic conditions previously described in the method. It can be seen a peak that corresponds to the excess of hydrogen peroxide used in the oxidation. To minimize it, was necessary to find the optimum hydrogen peroxide concentration that would produce complete sulfite oxidation and would not interfere with the sulfite peak. This concentration was established at 1 ml of 0.3% hydrogen peroxide each 10 ppm of sulfite to be oxidized.

Then it was considered necessary to change the distillation conditions established in our laboratory in order to determine sulfite by Iodimetric tritation, since there were chromatographic interferences with the chlorides. Therefore, different quantities and concentrations of HCl were tested to liberate standard sulfite, and they were collected in different alcaline solutions. Table 1 shows the recoveries obtained as the HCl and NaOH quantity or concentration was modified, as well as the influence from the oxidation time.

As Table 1 shows, the best recoveries were obtained when 3 ml of HCl 37% were used, and the destillate was collected in 0.5 ml of NaOH 1N. A minimum of between 2 and 3 hours being necessary to obtain a good oxidation.

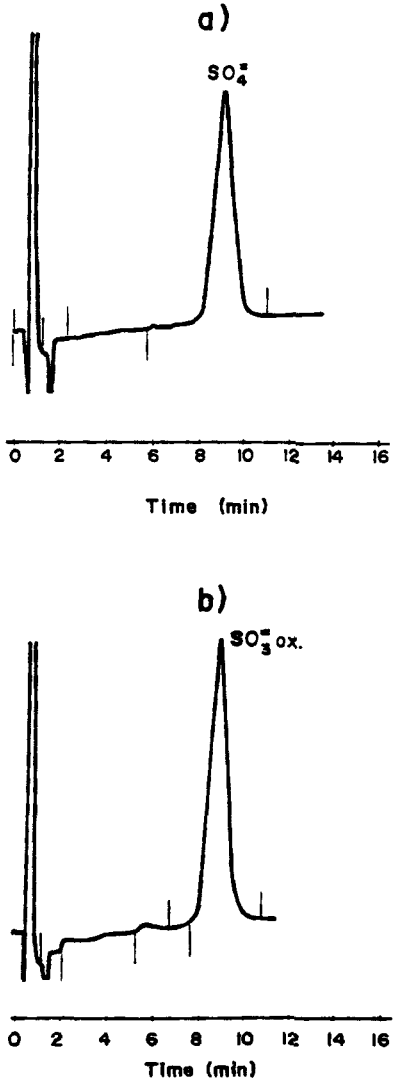

FIGURE 1.- Chromatograms of (a) sodium sulfate and (b) sodium sulfite oxidized (10 μg/ml respectively). Conditions: Waters IC-Pak anion column with Sodium Borate/Gluconate pH 8.5 eluent; conductivity detection; flow-rate: 1.2 ml/min; injection volume: 100 μl.

TABLE 1

Percentage Recovery of Sulfite (a) from standards after acid distillation.

Sulphite (ppm)	HCl (ml)	OHNa 1N (ml)	Oxidation time(hours)	Recovery (%)
20	7(HCl 37%)	5	1/2-1	*
20	1(HCl 37%)	5	1/2-1	<10
20	3(HCl 37%)	5	1/2-1	58
20	3(HCl 37%)	0.5	1/2-1	67
20	3(HCl 37%)	0.5	2-3	91
20	3(HCl 37%)	0.5	12	92

* chloride peak masked the sulfate peak
(a) average of four determinations

A linear regression analysis of the relationship between peak area versus amounts of standards was carried out within the range 0.5-100 μg/ml. The regression line obtained was y= 0.72x+0.08, with a correlation coefficient of 0.999.

The detection limit was 0.5 μg/ml under the chromatographic conditions described, although it could be lower when operating at higher sensitivity.

The mean recoveries of standards in the range 1-100 μg/ml was 90.4% (σ=17,04; n=14).

Recovery studies were performed on canned vegetable samples by adding known quantities of sodium sulfite to the sample solution prior to the distillation step. The results are given in Table 2, which indicates that satisfactory recoveries were achieved for the samples tested.

Some typical chromatograms obtained with samples of sausages (a), shrimp (b) and asparragus (c), are presented in Figure 2.

To establish whether the method is applicable to determine sulfite levels in foods, a number of samples representing a variety of foodstuffs were analyzed and compared with the modified Monier-Williams distillation technique developed in our laboratory. Table 3 shows data generated using both, the Ion-chromatographic and Monnier-Williams procedures.

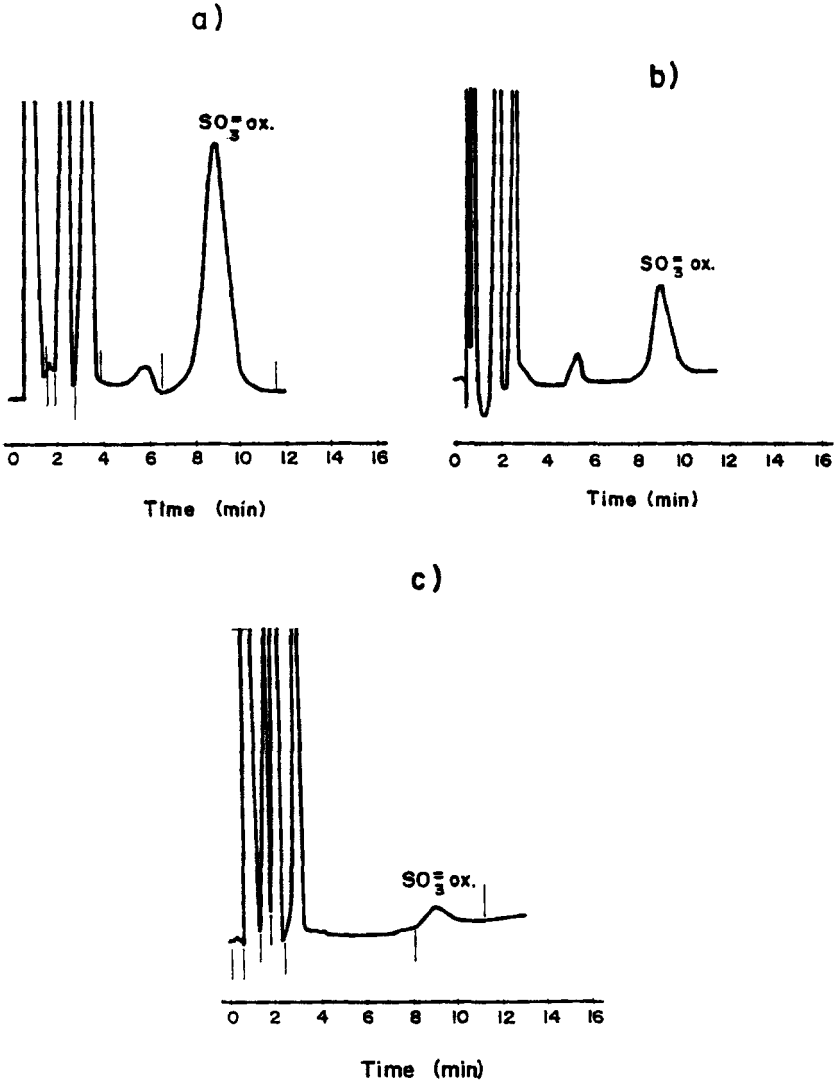

FIGURE 2.- Chromatograms obtained with: a) sausages (136 μg/g); b) shrimp (70 μg/g); c) asparragus (7 μg/g), using the proposed chromatographic method.

TABLE 2

Percentage recovery of sulfite from canned vegetable foods after acid distillation and oxidation to sulfate by IC analysis.

FOOD	Sulfite present in food (μg/g)	Sulfite added as sod. sul. (μg/g)	Sulfite found (μg/g)	Recovery (%)
Tomato	<1	50	38	76
id.	<1	100	83	83
Asparragus	16	50	49	74
id.	16	100	81	70
Artichoke	<1	20	14	70.5
id.	<1	50	42	84
id.	<1	100	87	87

Mean= 77.6%; n= 14; S.D= 6.65%

TABLE 3

Comparison of Ion Chromatography and Monier-Williams method for determining sulfite in foods.

	Sulfite, ppm (as SO_2) (a)	
FOOD	IC	M-W
Sausage 1	254	302
id. 2	313	383
id. 3	209	242
Juice	6	20
Canned mushroom	22	39
Shrimp	47	57
Canned artichokes	12	18
Tomato sauce	9	25

(a) Average of three determinations

The resulting concentrations of the method were comparable to those obtained by the modified Monnier-Williams method. The results, however, under the modified M-W method are considerably higher than those under the IC method. The fact that the acid-base tritation in the M-W method is nonspecific could be one reason for these results; any volatile acid may produce a positive interference depending on the nature of the samples.

To sum it up, our improved IC procedure combines the chemical approach of the Monnier-Williams technique with the superior detection system available through Ion Chromatography. The method permits quantitation at low parts-per-million and is not subject to the interferences associated with the Monnier-Williams procedure.

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