

Short Communication
Sulphite stabilizer in ion chromatography

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Abstract

The stability of sulphite in various stabilizers has been studied in ion chromatography. Sulphate–formaldehyde was the most stable system towards air oxidation. However, its retention was very weak in weak acidic eluent. Sulphite–methanol was also stable for at least 48 h towards air oxidation in the absence of metals such as iron.

1. Introduction

Sulphite is an interesting but difficult to determine anion because it is very unstable and is readily oxidized to sulphate in aqueous solution. The addition of formaldehyde [1–3], acetone, alcohols [1], glycerol [4], triethanolamine [5], etc., to prevent this oxidation has been proposed. Sulphite reacts with formaldehyde and is stabilized as hydroxymethanesulphonate, which is stable towards air oxidation and hydrolysis in slightly acidic solutions [6]. Formaldehyde has been widely used as a sulphite stabilizer.

Ion chromatography [1,3–9] has been reported for the determination of sulphite, including methods with no stabilizer [7] and with formaldehyde as a stabilizer [1,8]. Sulphite standard solution prepared from sodium hydroxymethanesulphonate has also been reported [6,9]. However, it has been found that formaldehyde affected the peak height obtained with an eluent not containing formaldehyde [3]. The efficiency

of sulphate stabilizer has also been reported to be in order carbonyls > alcohols = saccharides [1], triethanolamine > EDTA [5] or formaldehyde > glycerol and fructose [3].

Formaldehyde sulphite stabilizer can be determined only in basic solution by ion chromatography, because in basic solution hydroxymethanesulphonate decomposes to give sulphite ion [6], but in neutral or acidic solution it does not decompose and its retention time is very short in ion chromatography with a neutral or acidic eluent.

In this paper, the stability of sulphite with various stabilizers was examined with respect to storage period and temperature and the effect of foreign ions (especially metal ions which act as a catalyst of the oxidation). In ion chromatography with 1 mmol l⁻¹ phthalate (pH 6.0) as eluent, hydrogensulphite and hydroxymethanesulphonate ions, in the presence of formaldehyde as a stabilizer, are present and hydroxymethanesulphonate elutes very near to the solvent front. The degree of oxidation of sulphite (or conversion into sulphate) was calculated from

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the determination of sulphite and of sulphate (formed from the oxidation of sulphite).

2. Experimental

The ion chromatographic equipment consisted of a pump (CCPD; Tosoh), a variable-wavelength ultraviolet detector (UV-8000; Tosoh) monitoring at 255 nm, an injector (Rheodyne) with a 100- μ l sample loop, a column oven (CO-8000; Tosoh) maintained at 35°C and a pen recorder (YEW Type 3066; Yokogawa).

All chemicals were of analytical-reagent grade and deionized, distilled water, further filtered through a 0.45- μ m membrane filter, was used throughout. Standard sulphite solution was prepared from sodium sulphite and 5% (v/v) of various stabilizers. The stabilizers were used as received. Standard sulphate solution was prepared from sodium sulphate. The eluent was 1 mmol l⁻¹ phthalate, adjusted to pH 6.0 with dilute sodium hydroxide solution and filtered through a 0.45- μ m membrane filter before use.

Separation columns were prepared from 50 ×

4.6 mm I.D. columns packed with ODS resin (Capcell Pack C18, AG120, particle size 5 μ m; Shiseido) and then coated with cetyltrimethylammonium bromide (CTAB). The ion-exchange capacity of the coated column was about 0.15 mequiv. per column for phthalate ion. Both sulphite and sulphate were determined and the conversion to sulphate from sulphite was calculated.

3. Results and discussion

Methanol, formalin (37% aqueous formaldehyde solution), glycerol, acetone, ethanol and triethanolamine were tested as sulphite stabilizers. The conversions to sulphate from sulphite are given in Table 1 and a typical chromatogram is shown in Fig. 1. It was found that 20% of sulphite was converted into sulphate after 6 h and 100% after about 48 h in aqueous sulphite solution with no stabilizer. A 5% concentration of formalin (about 2% as formaldehyde) was allowed to be present in sulphite (in practice, present as hydroxymethanesulphonate) for more

Table 1
Effect of stabilizers on the conversion of sulphite into sulphate

Stabilizer		Conversion into sulphate (%)					
Compound	Concentration (%) ^a	6 h	24 h	48 h	3 days	7 days	14 days
None	–	20.0	65	80	–	100	–
	– (a)	–	–	5.0	–	52	90
	– (b)	–	–	25.0	–	32.0	50
Methanol	1.0	<0.1	<0.1	<0.5	1.1	2.8	10.3
	5.0	<0.1	<0.5	–	<0.5	2.0	4.0
	5.0(a)	–	<0.1	<0.5	–	<0.5	<0.5
	5.0(b)	–	–	<0.5	–	<0.5	<0.5
	5.0(c)	–	30	40	–	–	100
Formalin	10.0	<0.1	<0.1	<0.1	–	5.7	–
	5.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	5.0(a)	–	<0.1	<0.1	–	<0.1	<0.5
	5.0(b)	–	<0.5	1.0	–	–	1.0
Glycerol	5.0	–	7.8	–	17.0	48	50
Acetone	5.0	<0.5	<0.5	–	0.7	0.7	0.7
Ethanol	5.0	<0.5	2.7	–	7.7	15.0	15.5
Triethanolamine	5.0	<0.1	1.5	–	–	3.0	3.0

^a Storage temperature: (a) 4°C; (b) 50°C; (c) in a freezer; all others, room temperature.

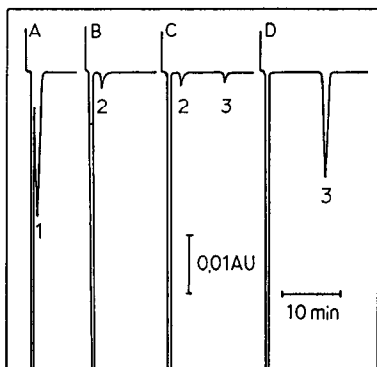


Fig. 1. Chromatogram of sulphite and sulphate with formalin and methanol as stabilizers. Sulphite $10 \mu\text{g ml}^{-1}$ in (A) 1% formalin, (B) 1% methanol, (C) aqueous solutions; (D) sulphate $10 \mu\text{g ml}^{-1}$ in aqueous solution. Eluent, 1 mmol l^{-1} phthalate (pH 6.0); flow-rate, 1 ml min^{-1} ; detection wavelength, 255 nm. Peaks: 1 = hydroxymethanesulphonate; 2 = sulphite; 3 = sulphate.

than 2 weeks at room temperature. However, the retention time of hydroxymethanesulphonate was shortened (to 2 min) and this peak was overlapped by many other peaks (e.g., chloride, formate) and was very near the solvent front in this chromatographic system. Sulphite was almost completely stable in 1–10% methanol solution for at least 48 h. Glycerol and ethanol as stabilizers were undesirable. Although acetone stabilized sulphite, the stability of acetone–sulphite was weaker than that of formalin–sulphite. Sulphite in triethanolamine was not detected owing to the interference of the large triethanolamine peak in this chromatographic system. Therefore, only sulphate converted from sulphite was determined. The retention times of sulphite in methanol, ethanol and glycerol were almost the same as that of sulphite (3.5 min) in

Table 2
Effect of foreign ions on the conversion of sulphite into sulphate

Ion	Added (μg)	Conversion into sulphate (%)			
		Methanol	Formalin	Glycerol	Acetone
Cl^- as NaCl	1000	<0.1	<0.1	<0.5	<0.5
NO_3^- as NaNO_3	1000	<0.1	<0.1	<0.5	<0.5
NO_2^- as NaNO_2	1000	<0.1	<0.1	<0.5	<0.5
Br^- as NaBr	1000	<0.1	<0.1	<0.5	<0.5
HCOO^- as HCOONa	1000	<0.1	<0.5	<0.5	<0.5
Fe(III) as FeCl_3	1000	95	1.0	93	100.0
	1	1.0	–	<0.5	<0.5
	1000 ^a	<0.1	<0.5	<0.5	<0.5
Mn(II) as MnCl_2	1000	100	1.5	88	15.1
	10	2.0	–	25.1	5.4
	1000 ^a	<0.1	<0.5	<0.5	<0.5
Cu(II) as CuCl_2	1000	50	<0.1	38.8	10.8
	10	60	–	–	–
	1	56	–	–	–
	1000 ^a	<0.1	<0.5	<0.5	<0.5
Zn(II) as ZnCl_2	1000	<1.0	<0.5	<0.5	<0.5
Al(III) as AlCl_3	1000	<0.5	<0.5	5.4	7.1
Mo(VI) as Na_2MoO_4	1000	3.0	–	–	–
Si(IV) as Na_2SiO_3	1000	30.0	<0.5	<0.5	<0.5
	100	1.0	–	–	–

Sulphite concentration: $25 \mu\text{g ml}^{-1}$ in 5% solution of each stabilizer.

^a After cation-exchange resin column.

aqueous solution. Sulphite with these stabilizers may be present as almost same species as in aqueous solution. In eluents of high pH, sulphite with formalin as stabilizer may also be present as sulphite ion and the separation of sulphite from the solvent front can be improved.

Whereas sulphite was liable to be converted into sulphate in methanol solution as stabilizer at high temperature (50°C), formalin stabilized sulphite at this temperature. However, both methanol and formalin prevented the conversion of sulphite into sulphate at low temperature (4°C) for at least 1 week and more than 1 week, respectively. With storage of sulphite–methanol in a freezer, greater stability of sulphite was observed.

The effect of the addition of typical anions and cations to sulphite solution in the presence of stabilizers was examined with respect to the conversion to sulphite after about 2 h. The results obtained are given in Table 2. Iron, manganese and copper cations accelerate the conversion from sulphite into sulphate in the presence of all the stabilizers except formalin. However, no conversion in the presence (1 mg) of zinc, aluminium and molybdenum cations and ascorbate, chloride, nitrate, nitrite and formate anions was observed in the presence of any of the stabilizers studied. When a sample solution containing iron, manganese or copper was passed through a cation-exchange resin column (Na⁺ form), no conversion was observed. Formalin as stabilizer prevented the conversion of sulphite into sulphate in the presence of iron, manganese or copper.

Sulphite–formaldehyde in the most stable system towards air oxidation and cations such as iron, as shown in Tables 1 and 2. However, formaldehyde is toxic and the retention of sulphite(–formaldehyde) was very weak with neutral and acidic eluents. Sulphite–methanol is stable for at least 48 h, but a sample should be passed through a cation-exchange resin for the determination of sulphite in environmental and biological fluids containing many cations (iron, copper, etc.) because sulphite with methanol as stabilizer was easily converted into sulphate in the presence of cations such as iron.

4. References

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