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Note

Sulfite–disulfite equilibrium on an ion chromatography column

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Sulfite compounds (including SO_3^{2-} , HSO_3^- , $\text{S}_2\text{O}_3^{2-}$ and SO_2) are widely used in industrial processes as antioxidants and preservatives. Their use in food products has come under closer scrutiny lately due to adverse physiological reactions in some individuals. Ion chromatography has been successfully used for determination of aqueous S^{IV} compounds in industrial mixtures^{1,2} and offers considerable advantages in time, sensitivity and selectivity over older methods^{3–5}.

In the course of investigating new eluents for the resolution of sulfite from sulfate using a commercial column, unexpected behavior was observed for the sulfite peak when certain eluents were used, namely, distortion of peak shape and shortened retention time with increased concentration. This behavior is described in terms of a sulfite–disulfite equilibrium occurring on the column. Conditions for a baseline resolution of sulfite and sulfate are also presented.

EXPERIMENTAL

All chromatograms were obtained on a Qic Analyzer ion chromatograph (Dionex, Sunnyvale, CA, U.S.A.) equipped with a 50- μl sample loop, an AG4 guard column, an AS4A ion separator column, a membrane-based background suppressor and a conductivity detector cell. The AS4A is a strong anion-exchange column, consisting of tetralkylammonium moieties bound to a polystyrene resin. The flow-rate was 2.0 ml/min, and eluents of various concentration were made from reagent-grade NaOH (Fisher), NaHCO_3 (MCB) and/or primary standard grade Na_2CO_3 (Thorn Smith), dissolved in 18-M- Ω water (Milli-Q system, Millipore, Bedford, MA, U.S.A.). Chromatograms were obtained on a strip-chart recorder, with retention times and peak heights measured manually.

A stock sulfite standard was made by dissolving *ca.* 0.6 g of reagent grade sodium bisulfite (Baker) in dilute aqueous formaldehyde [*ca.* 0.030 mol from 37% (w/w) aqueous formaldehyde; Mallinckrodt] and making up to 500 ml with high-purity water. The solution was standardized by oxidizing 5-ml aliquots in alkaline hydrogen peroxide (30%; MCB) and heating over a hot plate until excess peroxide was destroyed. These solutions were cooled, made up to volume and analyzed for sulfate by

TABLE I
CHARACTERISTICS OF SELECTED ELUENTS

Eluent No.	Chemical composition	pH	Ionic strength
1	$8.5 \cdot 10^{-3} M \text{HCO}_3^-$ $6.3 \cdot 10^{-4} M \text{CO}_3^{2-}$	9.19	$1.0 \cdot 10^{-2}$
2	$8.5 \cdot 10^{-3} M \text{HCO}_3^-$ $8.5 \cdot 10^{-4} M \text{CO}_3^{2-}$	9.30	$1.1 \cdot 10^{-2}$
3	$1.7 \cdot 10^{-3} M \text{HCO}_3^-$ $1.8 \cdot 10^{-3} M \text{CO}_3^{2-}$	10.26	$7.1 \cdot 10^{-3}$
4	$2.6 \cdot 10^{-4} M \text{HCO}_3^-$ $2.2 \cdot 10^{-3} M \text{CO}_3^{2-}$	10.70	$7.0 \cdot 10^{-3}$
5	$8.5 \cdot 10^{-5} M \text{HCO}_3^-$ $2.2 \cdot 10^{-3} M \text{CO}_3^{2-}$	10.75	$6.8 \cdot 10^{-3}$
6	$2.2 \cdot 10^{-3} M \text{CO}_3^{2-}$ $7.7 \cdot 10^{-4} M \text{OH}^-$	11.05	$7.5 \cdot 10^{-3}$

ion chromatography. A small sulfate contribution attending the unoxidized standard was subtracted from this value.

RESULTS

The composition data for six different eluents used in the study are given in Table I. At these pH levels, the form of aqueous S^{IV} will be sulfite (*i.e.*, 99% or greater). Capacity factors for five different anions are plotted for each of these eluents in Fig. 1. Note that in eluents 1 and 2 sulfite elutes after sulfate, while in the other eluents the order is reversed. Furthermore, the retention time for the sulfite peak in the first two eluents is concentration-dependent. The percent decreases in retention from eluent 1–6

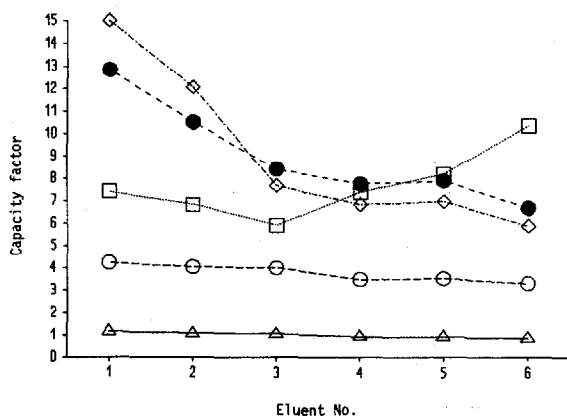


Fig. 1. Capacity factors for five anions using six different eluents. Δ = Chloride; \circ = nitrate; \square = phosphate; \bullet = sulfate; \diamond = S^{IV} .

are 23% for Cl^- , 21% for NO_3^- and 47% for SO_4^{2-} , *i.e.*, in approximate ratio to their charge.

In Fig. 2, chromatograms are shown for different concentrations of sulfite using eluent 1. Note that not only does the retention time shorten with increasing concentration, but the peak broadens abnormally and develops an asymmetric front tail. Similar behavior is observed with eluent 2, but to a lesser degree. Agreement of absolute retention times between different batches of eluent is variable, largely because of the sensitivity to small changes in the carbonate concentration.

These findings are consistent with the following series of reactions:

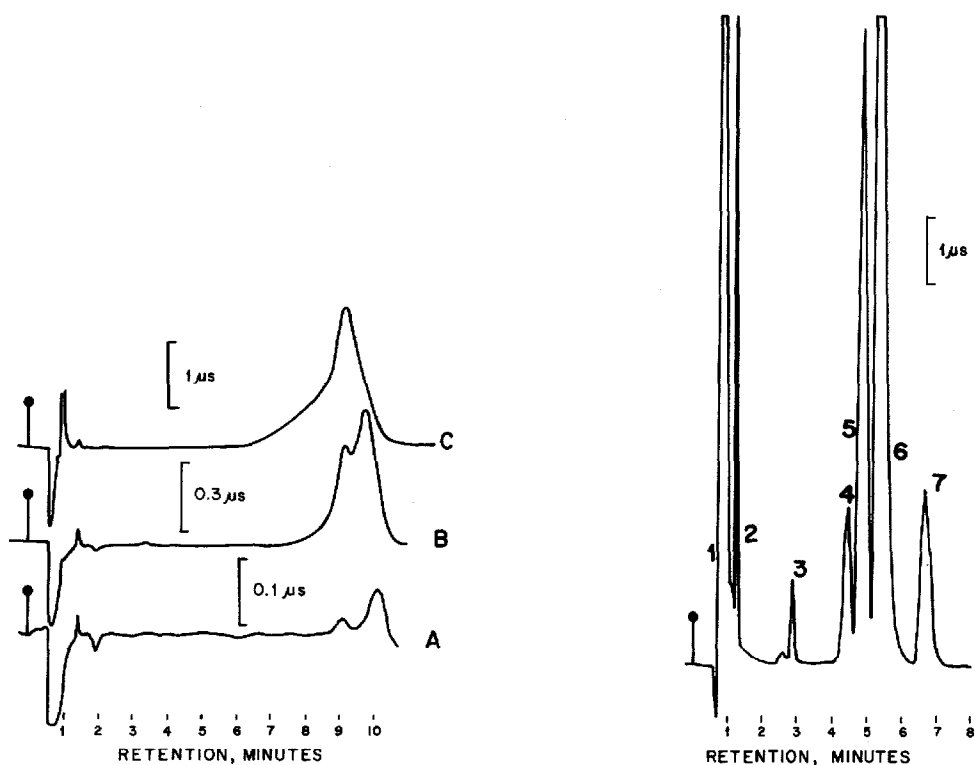
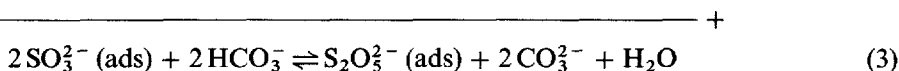
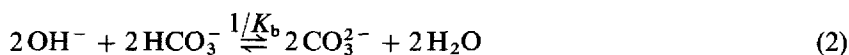
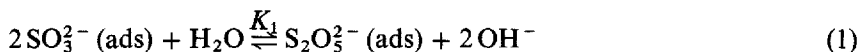


Fig. 2. Chromatograms of sulfate and "sulfite" as a function of sulfite concentration: (A) 1.2 ppm; (B) 11.6; (C) 46.4 ppm. Sulfate concentration is about 5% of sulfite values.

Fig. 3. Chromatogram of white table wine (25:1 dilution with 0.6 mg formaldehyde). Peaks: 1 = organic acids; 2 = chloride; 3 = nitrate; 4 = sulfite; 5 = sulfate; 6 = tartrate; 7 = phosphate.

Disulfite or pyrosulfite, $S_2O_3^{2-}$, forms in concentrated aqueous solutions of bisulfite ($K = 7 \cdot 10^{-2}$) (ref. 6), but not in solutions of sulfite. However, a reaction sequence such as described by reactions 1–3 could readily be facilitated by the conditions present in this experiment and is consistent with observations.

The hydrophobic yet positively charged stationary phase will support relatively high sulfite concentrations with the exclusion of water at the surface, favoring formation of disulfite. Disulfite, on the basis of mass-to-charge ratio, should elute earlier than sulfite, accounting for the concentration dependence of retention. The concentration and pH dependence of retention are also readily explained by the reaction sequence, whereas an alternative mechanism such as oxidation is inconsistent with observations. Formation of carbonate (as indicated in reaction 2) would increase its local concentration, inducing competition with sulfite and disulfite for surface absorption sites. Further reduction of elution time would result, and since this phenomenon is also dependent on the concentration of sulfite, the front-tailing is rationalized.

No concentration dependence of sulfite retention occurs for eluents 3–6, and of these, eluent 6 seems to offer the optimal situation with regard to sensitivity, rapidity and resolution of other common anions (see Fig. 1). A typical least-squares calibration curve using standards of 0.4, 1.7, 7.0, 29.0 and 116 $\mu\text{g/ml}$ (as HSO_3^-) gave the equation $y = 0.345x - 0.060$ ($r > 0.999$). Based on extrapolation from the lowest standard, a conservative detection limit of 0.8 ng of bisulfite is obtained. This sensitivity corresponds to 16 parts per 10^9 using a 50- μl sample loop; correspondingly lower limits are possible with larger sample loops.

A chromatogram illustrating the separation of sulfite from sulfate in a white table wine is shown in Fig. 3. Even though the sulfate peak is much larger (corresponding to $\approx 200 \mu\text{g/ml}$), the sulfite is sufficiently well resolved to permit an accurate analysis; simultaneous determination of tartrate and phosphate is also possible. At lower levels of sulfate and sulfite, the peaks are resolved at the baseline.

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