

Note

Zwitter ionic eluents for suppressed ion chromatography

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Since the introduction of suppressed ion chromatography¹, the eluents used for the analysis of anions have been limited to the original hydroxide, carbonate-bicarbonate and borate solutions. These alkaline eluents are not compatible with silica bonded columns, which in general display better resolution and a greater number of theoretical plates per meter than those based on styrene-divinylbenzene packings^{2,3}.

To make use of quaternary bonded⁴ and dynamically coated^{2,3} silica columns, eluents having a pH between 2 and 7 whose conductivity can be chemically suppressed are required. Zwitter ions, at their isoelectric point, do not respond to conductometric detection, some zwitter ions are also efficient buffers. These properties are used in suppressed ion chromatography of anions as shown in Fig. 1 using 2-(N-morpholino)ethanesulphonic acid (MES) as an example.

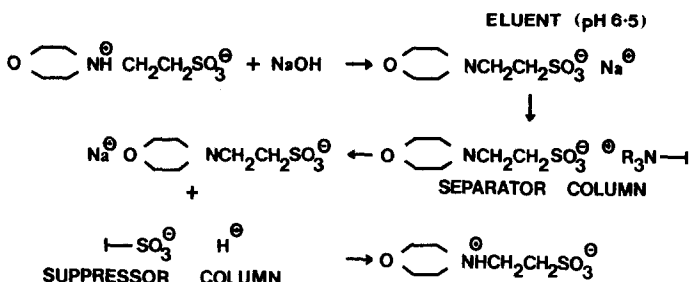


Fig. 1. Reaction scheme for the use of zwitter buffers in suppressed ion chromatography.

An eluent is prepared by addition of a slight excess of zwitter buffer to the sodium hydroxide solution. The resultant salt is used as eluent and competes for available anion-exchange sites with the sample anions. On entering the suppressor column the sodium ion is exchanged for that of hydrogen and the zwitter ionic form is restored. Sample anions elute in the acid form and are detected in a low conductivity background. The methodology should be equally applicable to cations using a strong base-weak acid zwitter ion and a hydroxide suppressor.

EXPERIMENTAL

Equipment

The chromatographic system consisted of the following elements: (1) a Waters M45 pump at flow-rate 2 ml min^{-1} ; (2) a Waters U6K variable volume injector; (3) a Wescan conductivity detector model 213A; (4) a Omniscrite recorder at chart-speed 0.25 cm min^{-1} .

Columns

Columns used included: (1) a Vydac 3021C 4.6 anion column (Edwards); (2) a μ Bondapak C_{18} column (Waters Assoc.); (3) a 030985 fast-run anion separator column (Dionex); (4) a 030829 anion suppressor column (Dionex).

Eluents

2-(N-morpholino)ethanesulphonic acid (MES) (BDH) and sodium hydroxide analytical grade (BDH) were combined to give a resulting solution 6 mM MES and 5 mM sodium hydroxide. Other as referred to in the text.

RESULTS AND DISCUSSION

Zwitter ionic eluents with bonded silica and organic anion-exchangers

The analytical scheme shown in Fig. 1 was used with MES sodium eluent, a quaternary ammonium bonded silica column (1) and a suppressor column (4). A chromatogram of a $100\text{-}\mu\text{l}$ injection of mixed anions is obtained in Fig. 2. Two interesting characteristics are tailing of the fluoride peak, due perhaps from interaction with unbonded silica, and the large separation between the singularly charged anions and the doubly charged sulphate.

In Fig. 3 a low-capacity styrene-divinylbenzene bonded anion-exchanger (3) has been substituted for the silica column. All conditions including injection volume and sample anion concentrations have been kept the same. The decrease in resolution may only in part be due to the column type, as this particular column had been in service for approximately six months. It can be noted however, that the similarities in retention times infer similar ion-exchange capacities. The water dip occurs between fluoride and chloride making quantitation difficult.

Dynamically modified octyl-decyl (C_{18}) bonded silica columns

There are two methods of coating non polar packings with cationic compounds. The first involves the "permanent" coating using large molecular weight quaternary ammonium compounds² and the second using lower molecular weight quaternary ammonium compounds added to the eluent³. While no real division exists between the two, the use of zwitter eluents with permanently coated C_{18} columns is equivalent to their use with bonded silica anion-exchangers. Surface modifiers such as tetrabutylammonium hydroxide which are added to the eluent, are used as their zwitter salts. Methanol or zwitter sodium salts may be added to adjust retention times. In Fig. 4 a 10-mM solution of tetrabutylammonium hydroxide (BDH) which has been neutralized to pH 6.5 with MES, has been used as eluent. The noise in this chromatogram is slightly worse than in Figs. 2 and 3 due to impurities in the tetra-

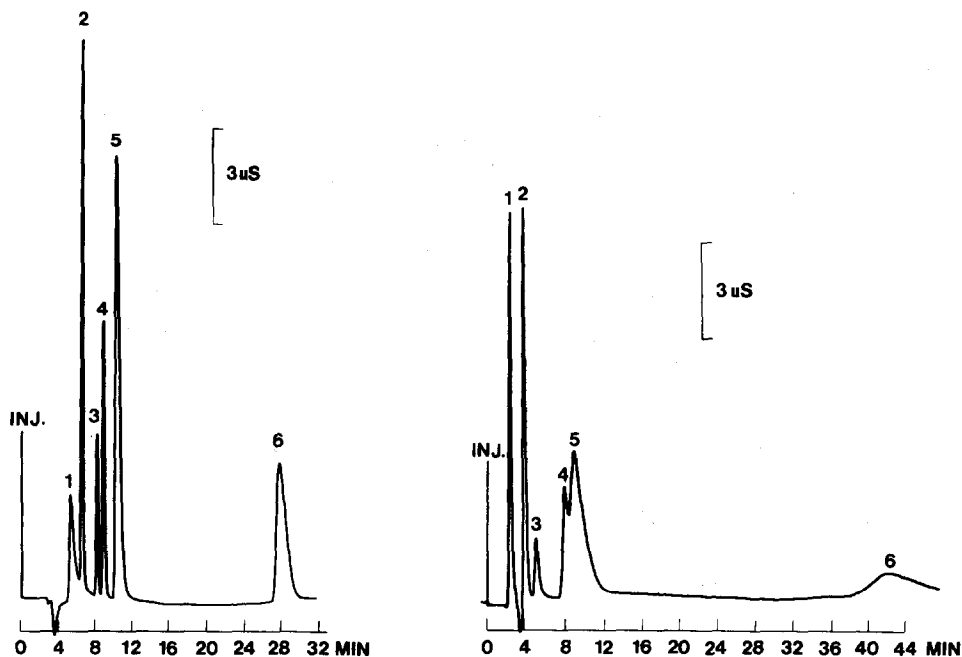


Fig. 2. Separation of sample anions on a quaternary ammonium bonded silica column (1). Experimental conditions: flow-rate 2 ml min^{-1} , eluent; 5 mM sodium hydroxide and 6 mM MES. Sample identification: 1 = $10 \mu\text{g ml}^{-1}$ fluoride; 2 = $10 \mu\text{g ml}^{-1}$ chloride; 3 = $10 \mu\text{g ml}^{-1}$ nitrite; 4 = $20 \mu\text{g ml}^{-1}$ bromide; 5 = $30 \mu\text{g ml}^{-1}$ nitrate; 6 = $20 \mu\text{g ml}^{-1}$ sulphate. Injection volume $100 \mu\text{l}$.

Fig. 3. Separation of sample anions on a quaternary ammonium bonded styrene-divinylbenzene column (3). Experimental conditions as for Fig. 2.

butylammonium hydroxide supplied. The resolution is superior to the previous figures due to a change in the relative retention of the anions. This change is possibly caused by the quaternary amine being surrounded by butyl groups rather than methyl groups. Such changes in retention behaviour may be of considerable use to the chromatographer.

Eluent regeneration

The significant cost of zwitter buffers makes recovery of used eluent an attractive proposition. This can be achieved by passing the used eluent through an anion-exchange column in the hydroxide form. Initially, the column becomes covered with zwitter and sample anions. After saturation, only sample anions exchange, releasing the zwitter ion. Only a short column is required as only sample and eluent impurities are retained. A column $10 \times 1 \text{ cm}$ I.D. packed with Amberlite IR-45 (OH^-) has given satisfactory service. This method can be used to purify the zwitter buffer prior to use, or to continuously recycle the eluent with addition of sodium hydroxide. Zwitter buffers refined in this way typically have conductivities of $5\text{--}10 \mu\text{S}$ after suppression compared to unrefined conductivities of $15\text{--}30 \mu\text{S}$.

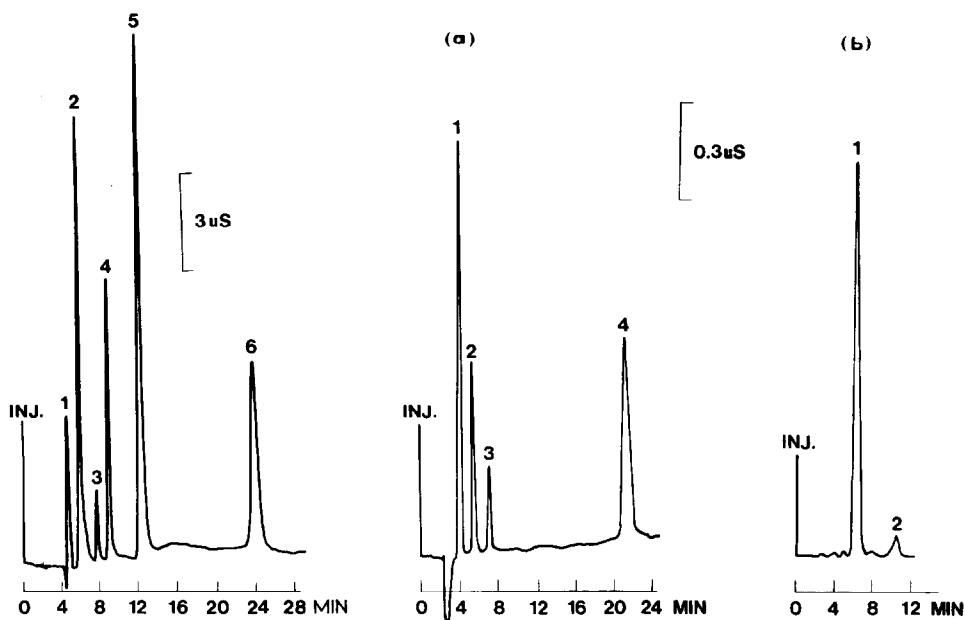


Fig. 4. Separation of sample anions on an octyl-decyl bonded silica column with ion-pairing reagent. Experimental conditions: eluent 10 mM tetrabutyl-ammonium hydroxide and 11 mM MES; other conditions as for Fig. 2.

Fig. 5 (a) Chromatogram of rainwater collected downwind of an aluminium smelter. 1 = Fluoride; 2 = chloride; 3 = nitrate; 4 = sulphate. Conditions as for Fig. 2. (b) Chromatogram of fluoride from Antarctic krill. 1 = Fluoride; 2 = chloride. Injection volume 25 μ l, eluent; 2 mM BES and 1.5 mM sodium hydroxide, chart speed 0.25 cm min⁻¹, columns (3) and (4).

Alternate zwitter buffers

As well as 2-(N-morpholino)ethanesulphonic acid (MES), NN'-Bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) and N-Tris(hydroxymethyl)methyl-2-aminoethanesulphonic acid (TES) have been used as their sodium salts. These singly charged anions are not very strong eluents in comparison with bicarbonate-carbonate mixtures and the availability of a doubly charged anion would be a useful addition to the range for use. N-(2-acetamido)iminodiacetic acid (ADA) disodium salt has been used, however complete protonation occurs in the suppressor column and the ADA is retained. A diamino-disulphonate is required.

Zwitter buffer eluents have been used in the analysis of rainwater, Fig. 5a and in the analysis of Antarctic krill for fluoride, Fig. 5b after an acid diffusion clean up procedure⁵.

Cation analysis should be possible using alkyl betaines with a general reversal of the methodology presented for anions.

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