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Clean-up procedure for the determination of inorganic anions by ion chromatography

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Abstract

Many organic anions can be strongly absorbed on ion chromatographic (IC) stationary phases, thus compromising analyses for inorganic anions. Selective removal of these organic anions from aqueous samples before IC was tried with four different types of SPE cartridges. An octadecylsilica cartridge loaded with cetyltrimethylammonium *p*-hydroxybenzoate was found to be effective in removing the tested organic anions without reducing the precision of analysis for common inorganic anions.

1. Introduction

Organic sulphonates are widely used as detergents, dyes and intermediates of dyes synthesis. Difficulties can arise when inorganic anions have to be determined in samples that also contain organic sulphonates. Although some application of ion chromatographic (IC) columns to the separation of mixtures organic anions have been reported [1], the eluents usually employed for the IC of common inorganic anions are not strong enough to elute organic anions, especially if multiply charged.

Fluctuations of the baseline, ghost peaks and rapid decreases in the column resolving power were encountered when common inorganic anions had to be routinely determined in samples of river water that was polluted by a dye factory. Regeneration of columns by washing with alkaline solutions or organic solvents was not successful, as the dark colour of the stationary phase resulted when a deteriorated column was examined. Guard columns were also tried, but organic pollutants quickly saturated them, probably because of the low ion-exchange capacity of the usual IC stationary phases.

Considering that similar difficulties can be met also when analyses of synthetic detergents or soft drinks have to be performed, a clean-up procedure capable of eliminating substances undesirable in IC could be of interest. Octadecylsilica coated with a cetyltrimethylammonium (CTMA) compound has already been employed as a stationary phase for IC [2,3]; a similar stationary phase was also used for the trace enrichment of organic anions in environment water samples [4]. Therefore, it seemed worthwhile to investigate whether such a stationary phase, or similar ones, would be suitable for the clean-up procedure needed. The results obtained by employing either silica or polymer-based C_{18} stationary

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phases, Quaternary Amine and Amino, are reported in this paper.

2. Experimental

2.1. Apparatus and reagents

A Metrohm (Herisau, Switzerland) Model 690 ion chromatograph equipped with a Hamilton PRP-X 100 column (150 × 4.1 mm I.D.) (Alltech, Deerfield, IL, USA) was used with 5 m*M* *p*-hydroxybenzoate (pH 8.6) as the eluent at a flow-rate of 1.8 ml min^{-1}. Both types of 100-mg C_{18} SPE cartridges used for this work were obtained from Alltech. Quaternary Amine and Amino cartridges were supplied by Baker (Deventer, Netherlands). Chemicals were obtained from Aldrich Italy (Milan, Italy).

2.2. Procedure

The following SPE cartridges were examined: Quaternary Amine, 500 mg; Amino, 500 mg; C_{18} silica, 100 mg loaded with CTMA; and C_{18} HEMA, 100 mg loaded with CTMA.

CTMA is absorbed on reversed-phase materials as an ion pair. To accomplish the purpose of this investigation, the counter anion of the absorbed CTMA should not be one of those sought by IC; *p*-hydroxybenzoate, which was adopted as a component of the IC eluent, was judged suitable. CTMA hydroxide and various CTMA salts are commercially available; considering their cost, a convenient procedure employing CTMA bromide was adopted. CTMA was deposited on C_{18} materials as its *p*-hydroxybenzoate salt by passing four times the following series of eluents: 5 ml of methanol; 10 ml of water; 10 ml of 1 m*M* CTMA bromide containing 10 m*M* sodium *p*-hydroxybenzoate; and 10 ml of 10 m*M* sodium *p*-hydroxybenzoate. After completing the CTMA loading procedure, the cartridges were dried by flushing them with air. Sodium *p*-hydroxybenzoate was prepared by neutralizing *p*-hydroxybenzoic acid solution with sodium hydroxide.

The test analytes were F^-, Cl^-, NO_2^-, Br^-, NO_3^-, HPO_4^{2-} and SO_4^{2-}, and the following organic anionic substances were chosen to test the effectiveness of the clean-up procedure: (A) 2-amino-1-naphthalenesulphonic acid, (B) 2-hydroxy-3,6-naphthalenesulphonic acid, (C) 2-anthraquinonesulphonic acid, (D) 2,7-naphthalenedisulphonic acid, (E) tartrazine (CI 19140), (F) Patent Blue V (CI 42051), (G) octylbenzenesulphonic acid, (H) dodecylbenzenesulphonic acid and (I) dodecyl sulphate.

Mixtures of compounds A–D, E–F and G–I were separately dissolved in ultra-pure water and added to solutions of inorganic anions in order to prepare three solutions containing 5 mg l^{-1} of each organic anion, while the concentrations of the seven inorganic anions ranged from 2 to 25 mg l^{-1}, in order to obtain chromatograms with uniform peak heights. Volumes of 10 ml of each of these three solutions were eluted on SPE cartridges to test the effectiveness of the clean-up procedure.

To test the dependence of organic removal on pH, the pH of the three standard solutions was adjusted with sodium hydroxide or *p*-hydroxybenzoic acid.

After clean-up, residual concentrations of organics were determined by appropriate techniques (HPLC for A–D [5], visible spectrophotometry for E and F and methylene blue extraction for G–I [6]).

3. Results

3.1. Removal of organic anions

Quaternary Amine and Amino cartridges removed organics quantitatively from solutions whose pH ranged from 3.5 to 12. Elution on both types of C_{18} cartridges produced complete removal in the pH range 4–8.

3.2. Recovery of inorganic analytes

Quaternary Amine silica proved not to be suitable for the purpose of this work, as it retained completely all anions other than chloride, and replaced them with the latter.

Table 1
Recoveries (%) of inorganic analytes ± standard deviations ($n = 4$)

Stationary phase	F	Cl	NO_2	Br	NO_3	PO_4^{2-}	SO_4^{2-}
Octadecylsilica	100 ± 1	100 ± 3	100 ± 1	98 ± 2	102 ± 1	97 ± 1	96 ± 1
C_{18} HEMA	100 ± 2	96 ± 6	98 ± 2	95 ± 2	98 ± 3	86 ± 6	83 ± 5
Amino	91 ± 4	106 ± 3	95 ± 3	91 ± 1	101 ± 3	16 ± 8	78 ± 9

The recoveries and their standard deviations ($n = 4$) for the remaining stationary phases are reported in Table 1. Singly charged anions were quantitatively recovered with C_{18} silica cartridges, while the concentration of multiply charged anions decreased slightly and reproducibly. C_{18} HEMA gave lower recoveries, with larger fluctuations, than C_{18} silica for all anions except fluoride. Amino cartridges retained considerable amounts of fluoride, phosphate and sulphate, and released chloride into test solutions.

Considering these results, octadecylsilica loaded with *p*-hydroxybenzoate was judged to be the most suitable for the purpose of this work among the stationary phases examined, and further experiments were carried out to test its performances.

3.3. Release of bromide ion from octadecylsilica cartridges

Considering that the bromide salt of CTMA was employed for loading the octadecylsilica stationary phases, an experiment was conducted to ascertain if bromide ion could have been released into eluted solutions. A 10-ml volume of a 25 mg l^{-1} solution of 2,7-naphthalenedisulphonic acid was passed through a treated cartridge and the eluted solution was analysed for bromide ion (detection limit 0.3 mg l^{-1}, signal-to-noise ratio = 3). Bromide ion was not detected.

3.4. Ion-exchange capacity

The maximum amount of organic substance that could have been absorbed was measured by eluting a 60 mg l^{-1} solution of Patent Blue V at pH 6.0. Up to 2.7 mg (4.7 μmol) of substance was retained by a C_{18} 100-mg silica cartridge, loaded with CTMA. For this anion, the breakthrough volume was larger than 50 ml.

3.5. Recycling of octadecylsilica cartridges

The CTMA loading and clean-up procedure employing C_{18} cartridges has been already employed for the trace enrichment of some aromatic sulphonic acids in water samples [4]. Good recoveries of those organic analytes have been obtained by washing the cartridges with methanol. Considering this, an experiment was carried out in order to ascertain if cartridges used once could have been employed for some further clean-up steps. CTMA loading and clean-up of standard solutions were repeated five times on the same group of C_{18} silica cartridges. It was found that, although the removal of organic substances was complete for all five clean-ups, the recoveries of inorganic analytes were reduced by about 5–10% if the cartridges were used more than twice.

3.6. Analysis of aqueous samples

Fig. 1 shows the chromatograms obtained for the analysis of two aqueous solutions after cleaning-up. Chromatogram A was obtained from a waste from the dye industry, which contained about 120 g l^{-1} of a mixture of aromatic sulphonic acids. A 5-ml volume of waste diluted 1:1000 was cleaned up and analysed. Chromatogram B refers to a 0.01% solution of a laundry detergent powder, containing sodium dodecylbenzene sulphonate, which was neutralized with *p*-hydroxybenzoic acid prior to analysis. As can be seen, in both chromatograms no

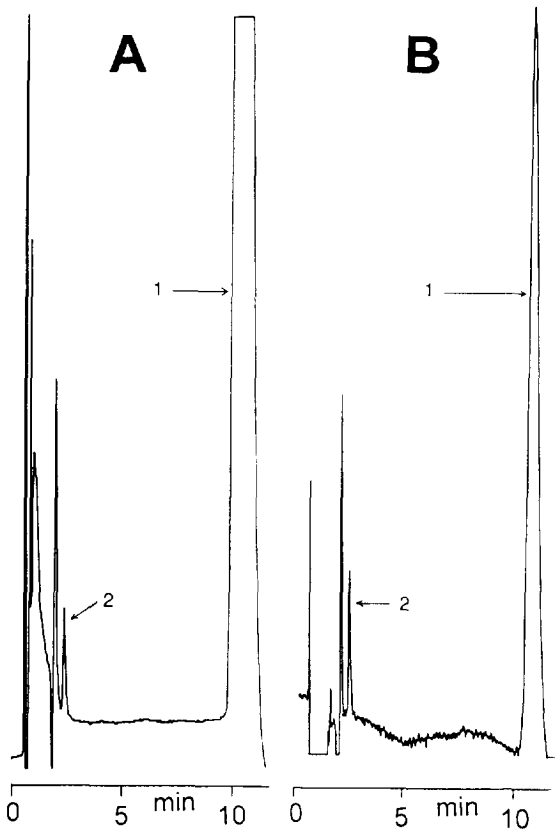

Fig. 1. Chromatograms of two cleaned-up aqueous samples. (A) Liquid industrial waste containing 120 g l^{-1} of a mixture of aromatic sulphonic acids (diluted 1000-fold); peaks: 1 = SO_4^{2-}, 300 mg l^{-1}; 2 = Cl^-, 0.87 mg l^{-1}. (B) 0.01% Solution of a laundry detergent powder (neutralized with *p*-hydroxybenzoic acid prior to clean-up); peaks: 1 = SO_4^{2-}, 13.5 mg l^{-1}; 2 = Cl^-, 0.17 mg l^{-1}.

peak is visible at 4.13 min, corresponding to the retention time of bromide ion under the conditions adopted. Quantitative calculations were based on peak height and an absolute calibration graph was employed. The 96% recovery of clean-up was taken into account for calculating the sulphate ion concentration in the original sample.

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