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Note

Dynamically coated columns and conductivity detection for trace determination of organic anions by ion chromatography

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Since the introduction of ion chromatography in 1975¹, it has become widely recognized that chromatography can be an attractive technique for the determination of inorganic anions, but because of a number of drawbacks a number of alternative chromatographic approaches have been investigated²⁻¹⁰. One approach of particular interest is the application of dynamically coated reversed phases^{2-4,7-8} where a hydrophobic modifier is allowed to equilibrate between the mobile phase and a hydrophobic reversed phase, and this modified phase is used to separate the inorganic ions.

Anionic modifiers such as sulfates and sulfonates, are used for the separation of cations^{2,7} and cationic modifiers, such as quaternary ammonium salts and tertiary amines^{2-4,7,8} for anions. Recent studies have shown that high-molecular-weight modifiers², which do not desorb in aqueous eluents, offer potential advantages for ion separations with low-conductivity eluents, and for trace enrichment where adjustment of the exchange capacities of the column and enrichment cartridge can be important.

Conductivity detection, which offers universal response for ionic substances, has not been used with most dynamically coated systems developed to date due to the presence of ionic modifiers and buffers. Low-conductivity weak-acid eluents, developed for use with low-capacity resins⁶, cannot be used with reversed-phase systems since they are adsorbed by the reversed phases and this ruins the anion separation. Consequently there is a need to develop dynamically coated systems that are more compatible with conductivity detectors. The main purposes of this work were: to develop dynamically coated systems compatible with conductivity detection; to improve dynamically coated systems where the modifier would not be desorbed into the mobile phase; and to examine the potential of these systems for trace enrichment.

EXPERIMENTAL

Apparatus

The chromatographic system consisted of a M6000A pump (Waters Assoc., Milford, U.S.A.), a Model 7125 injector (Rheodyne, Berkeley, CA, U.S.A.), and a conductivity detector (Laboratory Data Control, Riviera Beach, FL, U.S.A.). The conductivity detector was normally used in the differential mode where the detector output

was a percent of the background eluent conductivity. A large water bath (100 l) was used as a heat sink at ambient conditions to provide a constant column temperature.

Reagents and Materials

All eluents were made from HPLC grade solvents and all ionic modifiers and other reagents were reagent-grade chemicals. The tetrabutylammonium salicylate (TBA^+SAL^-) and tetramethylammonium salicylate (TMA^+SAL^-) eluents were prepared by neutralization of the hydroxide salts with salicylic acid. A 10- μm styrene-divinylbenzene phase (PRP-1; Alltech, Deerfield, IL, U.S.A.) was used throughout this study. "Permanently" coated columns were prepared by two techniques. Firstly, 1 l of $5 \cdot 10^{-4} \text{ M}$ cetylpyridinium chloride in 7 to 20% acetonitrile in water was pumped through the column and the sorbed cetylpyridinium was stabilized on the support with 500 ml of $5 \cdot 10^{-4} \text{ M}$ salicylic acid in acetonitrile-water (7:93). Secondly, a 10 to 40% acetonitrile solution in water that was $1 \cdot 10^{-3} \text{ M}$ in both cetylpyridinium chloride and salicylic acid was equilibrated with the column (1400 ml). These "permanently" coated phases were then equilibrated with eluents containing salicylate salts, such as tetramethylammonium salicylate. The amount of modifier was determined by evaporation and weighing the residue, or by UV spectrophotometric determination of the eluted salicylate (205 nm at pH 6) and cetylpyridinium (257 nm) ions.

RESULTS AND DISCUSSION

In previous studies² both octadecyl-bonded silica and styrene-divinylbenzene phases were used for the dynamic ion-exchange separation of inorganic anions. The styrene-divinylbenzene phase was used in these studies because of its superior pH sta-

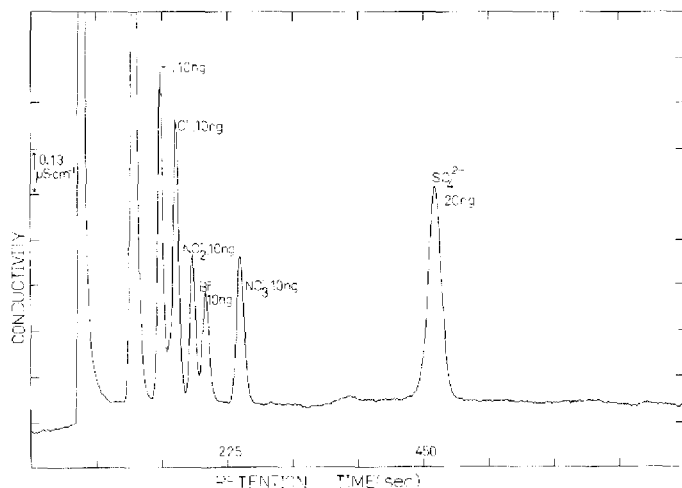


Fig. 1. Separation of anions with a tetrabutylammonium salicylate eluent and conductometric detection. Experimental conditions: 15 cm \times 4.1 mm I.D. PRP-1 column; eluent, $7.5 \cdot 10^{-4} \text{ M}$ TBA^+SAL^- in acetonitrile-water (7:93); flow-rate, $1 \text{ ml} \cdot \text{min}^{-1}$; pH, ca. 6.3; sample, 20 μl of $0.5 \mu\text{g} \cdot \text{ml}^{-1}$ F^- , Cl^- , NO_2^- , NO_3^- , and Br^- , and $1.0 \mu\text{g} \cdot \text{ml}^{-1}$ of SO_4^{2-} . Full-scale detector output was ca. 3% of eluent conductivity which was $38 \mu\text{S} \cdot \text{cm}^{-1}$.

bility; over a six month period this phase exhibited only a minor decrease in column efficiency.

Dynamically coated modifiers

Eluents such as phosphates or hydroxides of tetraalkylammonium ions have high conductivity, and will give a mixture of both positive and negative peaks with conductometric detection. However, hydrophobic eluents such as $\text{TBA}^+ \text{SAL}^-$ gave large column capacities at low concentrations, low background conductivity, and produced positive peaks for most anions of interest. Fig. 1 shows that excellent column efficiencies (height equivalent to a theoretical plate, HETP = 0.05 to 0.06 mm) and sensitivities can be obtained with this type of system. The poor separation of Cl^- and F^- is due to the presence of a small carbonate peak between them; all three components can be separated with baseline resolution with a $5 \cdot 10^{-4} M \text{TBA}^+ \text{SAL}^-$ eluent. Detection limits for the anions in Fig. 1 are in the range of 3 to 5 $\text{ng} \cdot \text{ml}^{-1}$ if a 200- μl sample is injected. This sensitivity is superior to that obtained with other single column systems. Two other hydrophobic modifiers, TBA^+ benzoate $^-$ and TBA^+ phthalate $^-$, were also studied and gave similar results.

One of the attractive features of these systems is its flexibility; modifier structure and eluent composition can be dramatically improved by an appropriate change in the experimental conditions.

Permanently sorbed modifiers

The modifier chosen for these studies was cetylpyridinium salicylate, and the range of coating weights studied was 10–80 mg per column volume (15 cm \times 4.1 mm I.D.). With salicylate eluents no appreciable change in retention times were observed after three weeks of constant use. A *ca.* $5 \cdot 10^{-4} M$ solution of $\text{TMA}^+ \text{SAL}^-$ in acetonitrile–water (7:93) was used for most separations. The separations obtained with the “permanent” coatings were comparable to that obtained with the $\text{TBA}^+ \text{SAL}^-$ system (Fig. 1) and column efficiencies were also similar. The capacity factors (k') observed for a series of anions separated on a column coated with 22 mg of cetylpyridinium ions were as follows: F^- , 2.0; HCO_3^- , 2.4; Cl^- , 2.5; BrO_3^- , 2.8; NO_2^- , 3.0; Br^- , 3.4; NO_3^- , 4.2; ClO_3^- , 5.8; SO_4^{2-} , 12.3; $\text{S}_3\text{O}_3^{2-}$, 15.6. Separation on these coated columns appears to be occurring by an ion-exchange mechanism because the modifier is not present in the mobile phase; all of the anions were eluted at the solvent front when the $\text{TMA}^+ \text{SAL}^-$ eluent was used with an uncoated column. Retention times increased when the non-aqueous content of the mobile phase was increased; this is the expected behaviour for the conventional ion-exchange systems. For dynamic systems the opposite effect was observed due to a reduction of sorbed modifier. Calibration curves were linear over the range studied (10 to 200 ng). The detection sensitivity obtained with these “permanently” coated columns was slightly less than that observed with dynamic systems.

With both the “permanently” coated and dynamic systems there was a slight increase in retention times (usually *ca.* 3%, maximum observed was 10% for a coated column) with increased sample weight for all the test anions, particularly at the lower concentration of the eluent ($5 \cdot 10^{-4} M$). The observed increase in k' values occurred even at very small sample sizes and thus it is unlikely that this effect is due to non-ideal chromatographic conditions (when [Sample] is not \ll [Eluent]). The exact cause of

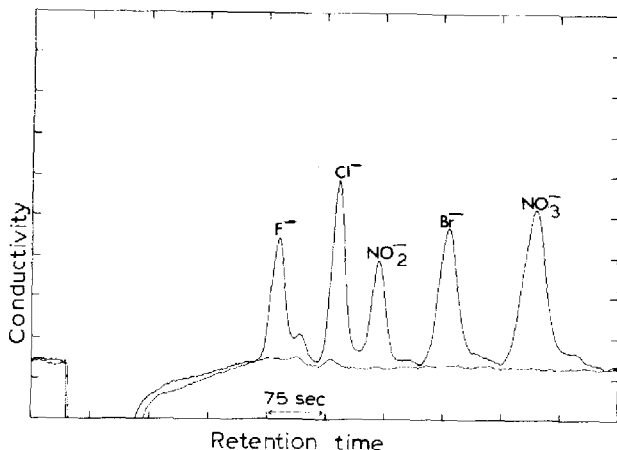


Fig. 2. Separation of anions after trace enrichment. Experimental conditions: eluent, $5 \cdot 10^{-4} M$ TMA⁺SAL⁻ at $1 \text{ ml} \cdot \text{min}^{-1}$; PRP-1 column coated with *ca.* 45 mg of cetylpyridinium chloride; sample, 2 ml of solution containing $50 \text{ ng} \cdot \text{ml}^{-1}$ of F⁻, Cl⁻, and NO₂⁻, and $150 \text{ ng} \cdot \text{ml}^{-1}$ of Br⁻ and NO₃⁻ enriched on a C₁₈ cartridge and then switched in-line. Full-scale detector output was *ca.* 10% of eluent conductivity which was $25 \mu\text{S} \cdot \text{cm}^{-1}$.

this increase in k' is unclear at present, but it may be related to the interaction between a polar anion and a hydrophobic surface; the effect was greatest for the most hydrophobic system studied (cetylpyridinium salicylate) and the hydrophobicity of the support would change as SAL⁻ ions are replaced by sample anions. More work is required to determine the cause of the observed increases in k' with sample weight. However, the observed changes in k' are not serious and do not limit the application of these techniques to trace anion analysis. Column efficiencies did not show the same dependence on sample size.

Trace enrichment

Trace enrichment was briefly examined with "permanently" coated columns and an example separation for a sample containing $50 \text{ ng} \cdot \text{ml}^{-1}$ of F⁻, Cl⁻ and NO₂⁻, and $150 \text{ ng} \cdot \text{ml}^{-1}$ of Br⁻ and NO₃⁻ is shown in Fig. 2. The HETP values calculated from the F⁻ to NO₃⁻ peaks were 0.13, 0.09, 0.08, 0.09, 0.09 mm, respectively, which is essentially the same as that obtained for a $20 \mu\text{l}$ sample; column efficiencies were normally better than this but this column had been used for several months and a slight decrease in column efficiency was observed. A comparison of trace enrichment with direct injection of $20 \mu\text{l}$ of a more concentrated sample showed that good recoveries were obtained over the range studied (1–10 ml) for the test anions. These results show that this system can be used for the determination of anions in low $\text{ng} \cdot \text{ml}^{-1}$ concentrations, and may be suitable for lower concentrations if larger samples are used.

The above results have shown that conventional high-performance liquid chromatography can be used with conductometric detection and dynamically coated reversed phases for the determination of $\text{ng} \cdot \text{ml}^{-1}$ and $\mu\text{g} \cdot \text{ml}^{-1}$ concentrations of inorganic anions. All of the necessary components are commercially available, and a wide range of eluents, column capacities, and modifiers are available.

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