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Note

Determination of inorganic anions at parts per billion levels using single-column ion chromatography without sample preconcentration

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Single-column ion chromatography using low-capacity ion-exchange columns and dilute eluents containing an aromatic acid[1–9] have proved to be a popular alternative to suppressed ion chromatography[10] for the determination of inorganic anions. The single-column methods appear to be readily adaptable to conventional high-performance liquid chromatography (HPLC) instrumentation and have been employed with conductivity[1–8], indirect refractive index[9], or indirect UV absorbance[8,9] detection methods.

Detection limits are comparable for the above detection methods and are typically in the range 0.2–1.0 ppm, depending on the particular ion being determined. Lower detection limits are possible if sample pre-concentration methods are employed[11], such as the use of an ion-exchange pre-column onto which a relatively large volume of sample is loaded before elution onto the analytical column. The utility of this sample pre-concentration procedure is strongly dependent on the sample composition, the procedure used to load the concentrator column, and preconditioning of the concentrator column. For example, samples containing a mixture of a strongly adsorbed ion (such as sulphate) and a weakly adsorbed ion (such as chloride) must be preconcentrated with care to avoid loss of chloride through displacement by sulphate.

One possible alternative to sample preconcentration is the use of large injection volumes (up to 2 ml), and this approach has been reported for the determination of chloride and sulphate using conductivity detection[2]. In our experience, conductivity detection is not optimal with large injection volumes due to severe baseline instability following injection. We have found that indirect UV absorbance detection[8,9,12] is superior and in this paper, we report the use of this detection method for the determination of a mixture of inorganic anions at low ppb* levels.

EXPERIMENTAL

The HPLC apparatus used consisted of a Waters Assoc. (Milford, MA, U.S.A.) Model M-6000A pump, Model U6K injector, Model M-480 variable-wave-

* Throughout this article, the American billion (10^9) is meant.

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length detector and Model M-730 data module. The pump was fitted with a high-sensitivity pulse dampener. A Bioanalytical Systems (Lafayette, IN, U.S.A.) Model LC-22A column heater was also used.

The low-capacity ion-exchange columns employed in this study were obtained from the Separations Group (Hesperia, CA, U.S.A.) and consisted of a Vydac 302 IC 4.6 column (250 × 4.6 mm I.D.) and a Vydac 302 IC 3.0 column (250 × 3.0 mm I.D.). The reagents used were of the highest available purity and standard solutions of the ions were prepared by dissolving the sodium salts in water purified on a Millipore Milli-Q water purification system.

Eluents were prepared by dissolving an appropriate amount of potassium hydrogen phthalate in doubly distilled water and adjusting the pH to the desired value with sodium hydroxide, using a calibrated pH meter. Eluents were filtered through a 0.45-μm filter and degassed in an ultrasonic bath before use. The eluent container was immersed in a temperature regulated water bath (35°C) and allowed to equilibrate before use. A portion of the eluent was used to fill the reference cell of the detector, using a 20-ml syringe.

Other experimental conditions are provided in the captions to the figures.

RESULTS AND DISCUSSION

Instrumental considerations

In view of the fact that maximum sensitivity was required in this study, special care was taken to optimize the performance of the equipment used. In this regard, one of the first steps taken was to fill the reference cell of the detector with eluent. This avoided the requirement for excessive electronic offset on the detector, which in this application was operating in a differential mode with the sample and reference cell absorbances balanced at a relatively high absorbance value (generally greater than 1.0 absorbance units). The elution of a solute anion resulted in a decrease in the eluent concentration in the sample cell, leading to a decrease in background eluent absorbance, which was displayed as a positive peak for that solute[9].

Selection of the detector wavelength was an important factor in the attainment of high sensitivity. A wavelength corresponding to a high molar absorptivity of the eluent provided a larger change in the absorbance of the eluent than if the chosen wavelength corresponded to a lower relative value of eluent absorptivity. A further factor to be considered was the baseline noise, which increased as the molar absorptivity of the eluent increased, due to reduced amounts of light reaching the photomultiplier. In practice, baseline noise was the limiting factor in the selection of a suitable wavelength, and we have found that 285 nm gave the best ratio of signal to noise. Lower wavelengths gave excessive noise, whereas higher wavelengths gave reduced signal. The selected wavelength of 285 nm corresponded to a local maximum in the absorption spectrum of phthalate, so that slight errors in setting of the wavelength would not cause significant changes in sensitivity.

Column efficiency and detector stability are enhanced when the eluent and column are maintained at the same elevated temperature. For this reason, careful attention was given to temperature control of both column and eluent. In addition, pump induced noise was minimised by use of a high-sensitivity pulse-dampening accessory and dead volume throughout the chromatographic system was reduced to

a minimum. The performance of the system was assessed with a Vydac 302 IC 4.6 column, using a 100-μl injection of a mixture of anions in the concentration range 2.5–7.5 ppm. The chromatogram obtained (Fig. 1) illustrates the efficiency of the chromatographic system (5200 theoretical plates for iodide, using the 5-σ method) and shows the expected level of baseline noise. The detection limits obtained here (*e.g.* 48 ppb for chloride) already represented a considerable improvement on that attained in previous reports[1–9], and this was attributed to the system modifications discussed earlier. A further notable feature of Fig. 1 was the appearance of a "system" peak which coeluted with sulphate under the mobile phase conditions used. This peak has also been observed by other workers[13,14].

Use of large injection volumes

Chromatograms obtained with injection volumes of 250 and 1000 μl, using the Vydac 302 IC 3.0 column, are illustrated in Fig. 2. In these chromatograms, the solvent peak was seen to increase in proportion to the injection volume and the system peak also showed a corresponding increase. In addition, Fig. 2 shows that use of a large injection volume caused a slight increase in retention of early eluting ions, but peak width and baseline stability were relatively unaffected by the injection volume.

The retention increase of early eluting peaks can be explained by the fact that as the aqueous sample enters the column, solute ions are strongly adsorbed onto the

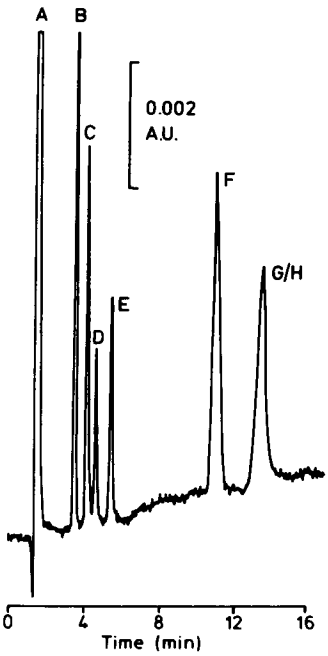

Fig. 1. Chromatogram obtained after optimizing the HPLC system for sensitivity. Conditions: column, Vydac 302 IC 4.6; eluent 5 m*M* potassium hydrogen phthalate at pH 4.0; flow-rate, 2.0 ml min^{-1}; detection, UV absorbance at 285 nm; sensitivity, 0.01 a.u.f.s.; injection volume, 100 μl. Peak identities and solute concentrations: A = solvent, B = Cl^- (2.5 ppm), C = NO_2^- (2.5 ppm), D = Br^- (2.5 ppm), E = NO_3^- (2.5 ppm), F = I^- (7.5 ppm), G = SO_4^{2-} (7.5 ppm), H = system peak.

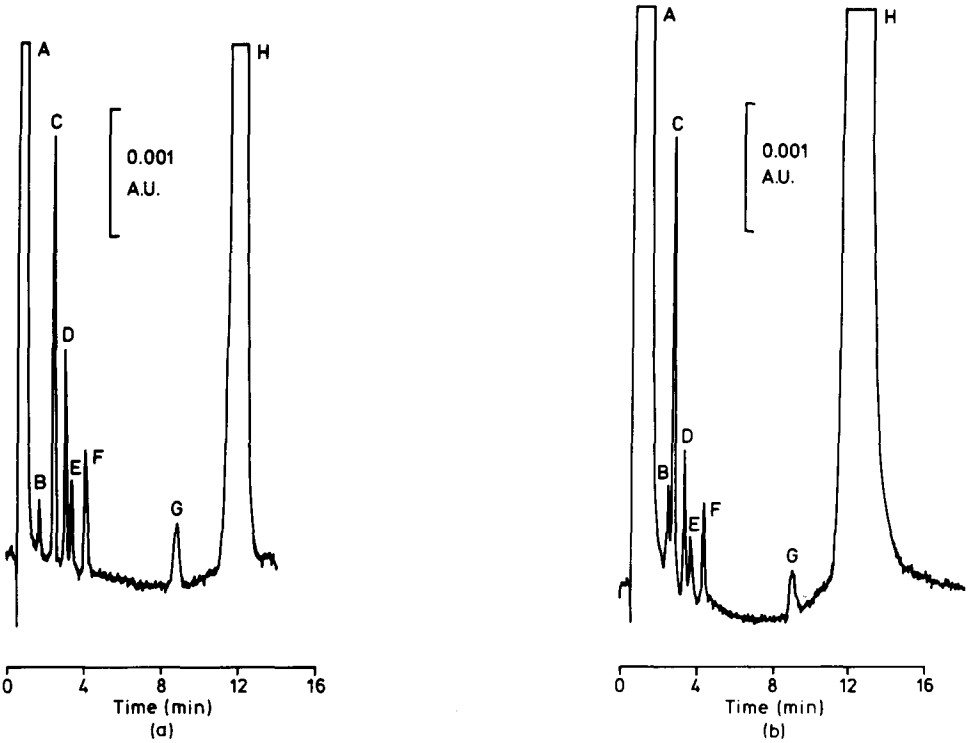

Fig. 2. Chromatograms obtained using large injection volumes. Conditions: column, Vydac 302 IC 3.0; eluent, 2.5 m*M* potassium hydrogen phthalate at pH 4.0; flow-rate, 2.0 ml min^{-1}; detection, UV absorbance at 285 nm; sensitivity 0.005 a.u.f.s., injection volumes (a) 250 μl, (b) 1 ml. Peak identities and solute concentrations: A = solvent, B = $H_2PO_4^-$ [(a) 100 ppb, (b) 50 ppb], C = Cl^- [(a) 400 ppb, (b) 120 ppb], D = NO_2^- [(a) 288 ppb, (b) 60 ppb], E = Br^- [(a) 250 ppb, (b) 60 ppb], F = NO_3^- [(a) 280 ppb, (b) 60 ppb], G = I^- [(a) 300 ppb, (b) 80 ppb], H = system peak.

top of the column. Since these ions do not begin to move significantly until eluent ions exert a displacing effect, it follows that larger injection volumes will cause slightly longer retention times for some ions. The same rationale can be advanced to explain the observation that solute peaks were not appreciably broadened by the use of large injection volumes (compare Figs. 1 and 2). Here the solute ions become concentrated at the top of the column by adsorption from the aqueous sample and are effectively reinjected as a compact band when first contacted by eluent following the sample injection volume. Provided that the large injection volume does not destabilise the

TABLE I

DETECTION LIMITS OBTAINED BY SINGLE-COLUMN ION CHROMATOGRAPHY WITH INDIRECT UV ABSORBANCE DETECTION USING 1 ml INJECTION VOLUMES

Ion	*Detection limit (ppb)*
$H_2PO_4^-$	14.7
Cl^-	5.4
NO_2^-	8.3
Br^-	20.0
NO_3^-	11.5
I^-	30.8

baseline and the necessarily large solvent peak does not obscure early eluting peaks, then this approach can be extended to even larger injection volumes than shown in Fig. 2b.

Detection limits calculated from calibration data prepared using 1-ml injections of mixtures of anions are given in Table I. These values represent an approximately tenfold decrease on those calculated from Fig. 1 and illustrate the utility of large injection volumes for trace analysis by ion chromatography. The variation in detection limits for ions of similar retention can be attributed to the UV absorbance of some ions (NO_2^-, Br^-, NO_3^-, I^-) which partially offsets the decrease in background eluent absorbance for those ions, giving a smaller measured peak.

CONCLUSIONS

The determination of anions in the low ppb range by direct injection of large sample volumes is practical for some inorganic anions. This approach offers a viable alternative to sample preconcentration methods and requires only simple modification of conventional ion chromatographic instrumentation.

NOTE ADDED IN PROOF

Subsequent to submission of this paper, two further publications have appeared which deal with non-suppressed ion chromatography using Vydac columns. Willison and Clarke[15] have reported a procedure for the analysis of atmospheric aerosols using conductivity detection, and Alder *et al.*[16] have described a combined conductivity and permittivity detector which permits detection of chloride ion at less than 50 ppb using a 100-μl injection.

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