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Note

Rapid determination in water of chloride, sulphate, sulphite, selenite, selenate and arsenate among other inorganic and organic solutes by ion chromatography with UV detection below 195 nm

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Single-column ion chromatography, using silica bonded ion exchangers[1], is a well established technique for the separation of cations and anions[2]. The ions are detected indirectly through pairing[3] or marker[4–6] ions by UV absorption, conductivity or refractive index. Typical limits of detection are about 1 mg/l. Sensitivities down to μg/l level are in principle obtainable by pre-concentration methods[4]. For optimal sensitivity all these methods require a good control of the temperature of the detector and/or column. High-performance liquid chromatography (HPLC) of ions with direct photometric detection at wavelengths of 195–220 nm is much less influenced by temperature. Also broad vacancy peaks or system peaks due to the slow elution of dips in the concentration of the pairing or marker ions after sample injections, do not occur. This wavelength range is suitable for the direct detection of a number of anions (*e.g.* bromide, nitrite and nitrate)[6–9] at the μg/l level and many organic compounds *e.g.* organochlorines[9] and carboxylic acids[10–12] are easily detected. Chloride and sulphate among many other inorganic anions do not absorb sufficiently in the 195–220 nm range to be detectable[6,7,9]. However if the UV detector can be operated at wavelengths below 195 nm, chloride and sulphate become increasingly detectable and the sensitivity increases strongly for most other ions detectable in the 195–220 nm range.

Requirements for successfully operating the detector in this wavelength range are a sufficiently transparent eluent, displacement of dissolved oxygen and a low-UV-absorbing column bleed. These conditions can easily be met when using a silica-bonded anion exchanger[1] and eluting with a phosphate buffer. The simplicity, versatility and sensitivity of high-performance ion chromatography with direct UV direction below 195 nm is demonstrated in this paper for a range of inorganic and organic compounds.

EXPERIMENTAL

A stainless-steel (SS316) column of 25 × 0.4 cm I.D. containing a silica-bonded quaternary amine (Vydac 302 ion chromatography column; Vydac Separations Group, Hesperia, CA, U.S.A.) was used for the separations. A new column was eluted with 0.1 *M* phosphate at pH 5.5 until the baseline of the detector was within

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back-off range at the most sensitive setting (0.0025 AU) at 190 nm. This took about 48 h at a flow-rate of 2 ml/min. Eluent was pumped through the system with an ETP-Kortec K35 M HPLC pump (ETP-Kortec, Sydney, Australia). Samples were injected with a Rheodyne 7125 high-pressure sampling valve. All samples were passed through a 0.45-μm filter (type SM11306, Sartorius, Göttingen, F.R.G.) immediately before injection. The effluent was monitored at between 170 and 200 nm with an ETP-Kortec K95 variable-wavelength UV detector. Organic acids were determined simultaneously with chloride, bromide, nitrite, nitrate as well as selenite and arsenate, eluting with 0.01 – 0.03 *M* phosphate at pH 3.8. Iodide, sulphate, sulphite and selenate were determined in *ca.* 0.02 *M* phosphate at pH 4.8. pH was adjusted by adding phosphoric acid to solutions of dipotassium hydrogen phosphate or potassium dihydrogen phosphate. All chemicals were of high-purity grade (BDH Aristar). Solutions were made up in double quartz distilled water.

RESULTS AND DISCUSSION

In Fig. 1 the simultaneous separation of trace amounts of carboxylic acids and inorganic anions is shown for a detector wavelength of 190 nm. Optimization for these ions with regards to the required time of separation, resolution, background signal, detector noise and maximum salinity allowed in the sample, was done by varying the flow-rate, pH and phosphate concentration of the eluent and the detector wavelength. A compromise was reached using a wavelength of 190 nm, flow-rate of 2 ml/min, phosphate concentration of 0.01–0.03 *M* and a pH range of 3–5. The Vydac

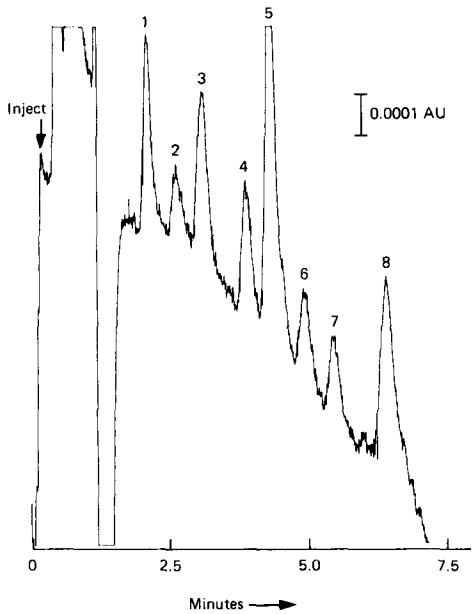

Fig. 1. Separation of 10^{-5} *M* each of acetate and propionate (1), butyrate (2), lactate (3) and formate (4), 0.72 mg/l chloride (5), 10 μg N/l of nitrite (6) and nitrate (8), 20 μg/l bromide (7). Conditions: column Vydac, 302-IC 4.6; eluent, 0.02 *M* potassium dihydrogen phosphate pH 3.8; flow-rate, 2 ml/min; UV detector wavelength, 190 nm; detector attenuation, 0.00125 AU; injector volume, 100 μl.

column gave a low-UV-absorbing bleed up to a pH of 5, above which it increased exponentially.

The effect of flow-rate is shown in Fig. 2. The decrease in resolution with increasing flow-rate is clearly seen for selenite and arsenate (peaks 5 and 6) and for formate and succinate (peaks 7 and 8). The effects of wavelength on noise and sensitivity of the detector is shown in Fig. 3 for a wavelength range of 170–210 nm. Due to the decreasing energy output of the deuterium lamp the noise level increases rapidly below 190 nm. The sensitivity decreases with increasing wavelength for all compounds, especially for acetone (peak 1 in Fig. 3), selenite (peak 5), chloride (peak 9) and bromide (peak 11).

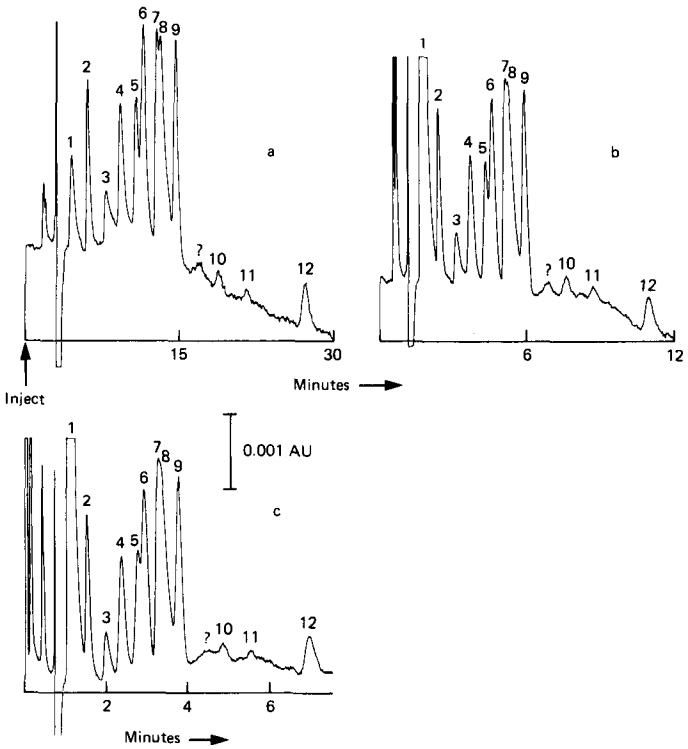

Fig. 2. Effect of flow-rate on the separation of a mixture of 0.01% *n*-butanol (peak 1 in a), 0.01% acetone (peak 1 in b and c), 10^{-4} *M* each of acetate plus propionate (2), butyrate (3), lactate (4), formate (7) and succinate (8), 1 mg/l Se as selenite (5), 1 mg/l. As as arsenate (6), 5 mg/l chloride (9), 10 μg N/l each of nitrite (10) and nitrate (12), 10 μg/l bromide (11). Conditions: eluent, 0.01 *M* phosphate (pH 3.7); wavelength, 175 nm; detector attenuation, 0.005 AU; injection volume, 100 μl; flow-rate, 0.8 ml/min (a), 2 ml/min (b) and 3.2 ml/min (c).

The effect of pH on the retention times and resolution is shown in Fig. 4 for succinate and a range of inorganic anions. The retention of selenate and succinate is strongly influenced by pH. For some anions and all organic acids used sensitivity decreases with decreasing pH, shown in Fig. 4 for succinate (peak 3), nitrite and

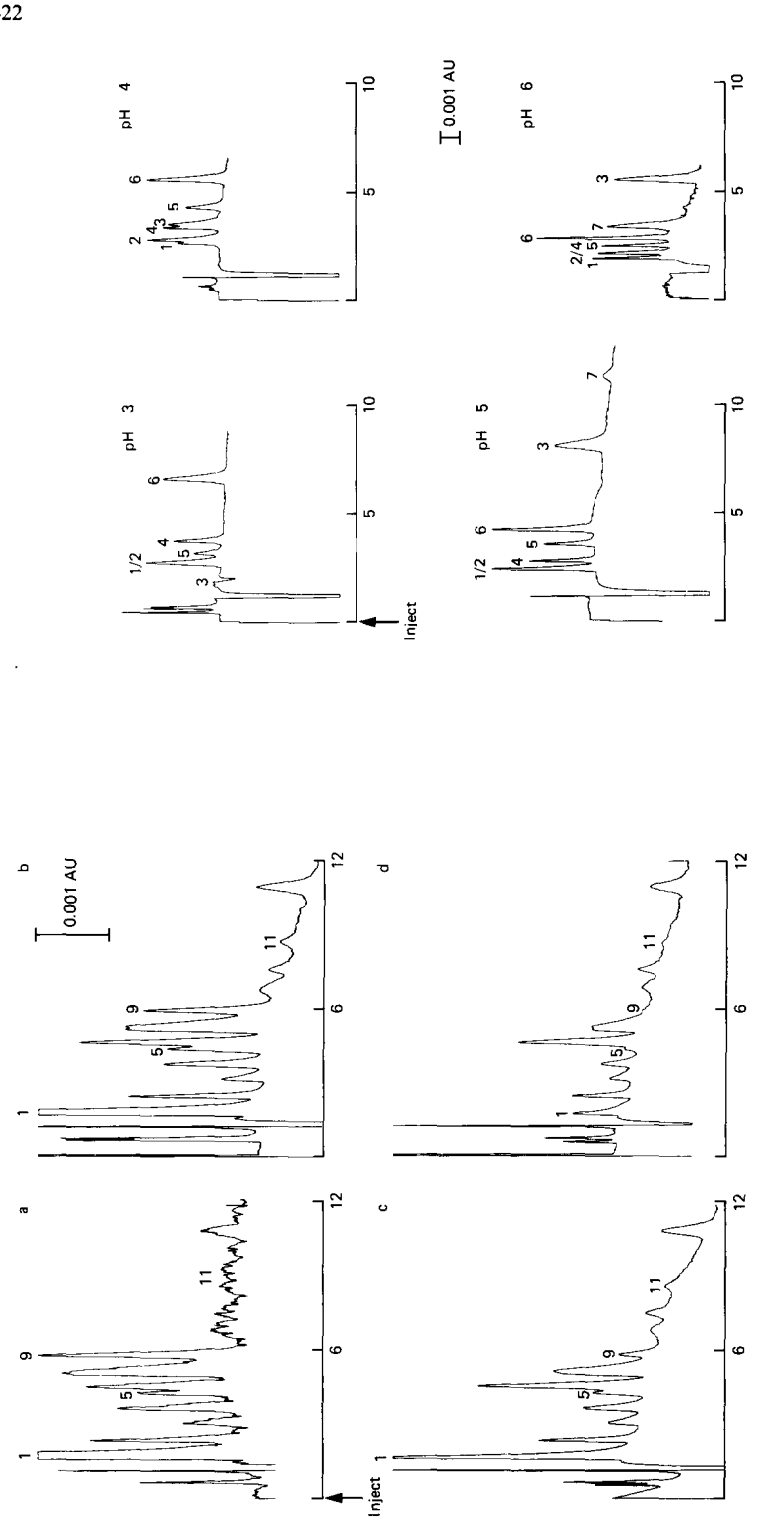

Fig. 3. The effect of wavelength on detector noise and sensitivity. The mixture of Fig. 2 was run at 170 nm (a), 190 nm (b), 200 nm (c) and 210 nm (d). Conditions and peak identification as in Fig. 2b.

Fig. 4. The effect of pH on the resolution and retention times of 1 mg/l Se as selenite (1), 1 mg/l As as arsenate (2), 10^{-4} *M* succinate (3), 5 mg/l chloride (4), 0.1 mg N/l each of nitrite (5) and nitrate (6), 1 mg/l Se as selenate (7). Conditions: eluent, 0.025 *M* phosphate (pH 3.6); wavelength, 180 nm; detector attenuation, 0.02 AU; flow-rate, 2 ml/min; sample volume, 100 μl.

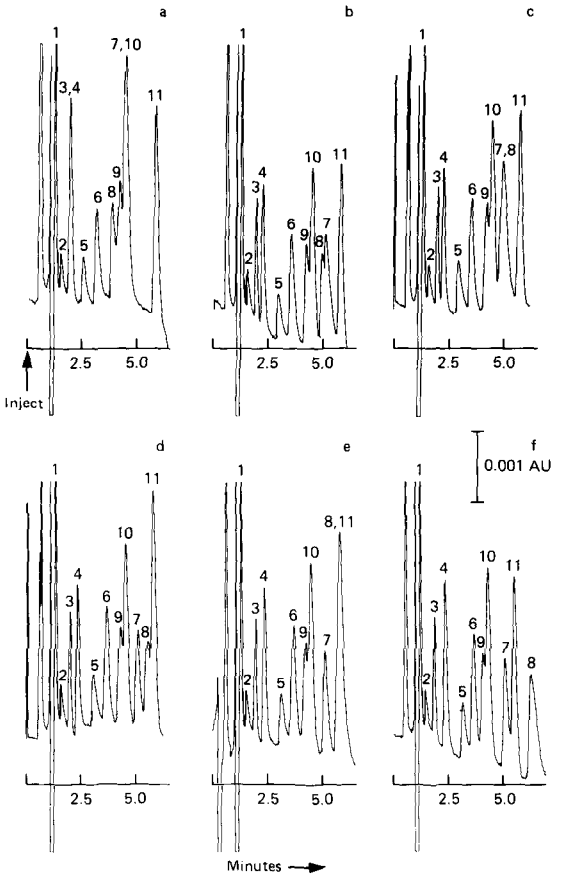

Fig. 5. The effect of pH on the resolution of 10^{-3} *M* glycerol (1), 0.01% *n*-butanol (2), 10^{-6} *M* phenol (3), 10^{-4} *M* phenol (3), 10^{-4} *M* each of acetate plus propionate (4), butyrate (5), lactate (6), formate (7), succinate (8), 1 mg/l Se as selenite (9), 1 mg/l As as arsenate (10), 5 mg/l chloride (11). Conditions: eluent, *ca.* 0.02 *M* phosphate, pH increasing from 3.55 (a) to 3.90 (f); wavelength, 180 nm; detector attenuation, 0.005 AU; flow-rate, 2 ml/min; sample volume, 100 µl.

selenate (peaks 5 and 7). At pH $\approx$3.8 most organic compounds and inorganic anions are reasonably resolved. This is shown in Fig. 5 for a pH range of 3.5–3.9. In this pH range iodide, sulphate, selenate and sulphite are however strongly retained (*e.g.* selenate in Fig. 4, peak 7) but can be better separated at a pH $\approx$ 4.8 (Fig. 6).

In Fig. 7 the elution of iodide at pH 4.8 is shown. Iodide could not be determined below 0.1 mg/l, which was surprising considering the sensitivity measured at the mg/l level. Removal of oxygen and nitrite from the sample gave some improvement, but below 0.1 mg/l iodide seemed to disappear rapidly from solution. The action of exo-enzymes in water samples, catalyzing the conversion of iodide offers a possible explanation for this[13], although traces of metals and organics in the HPLC system could be involved in the conversion of iodide.

Some organic acids, other than the acids shown in Figs. 1–5, were also inves-

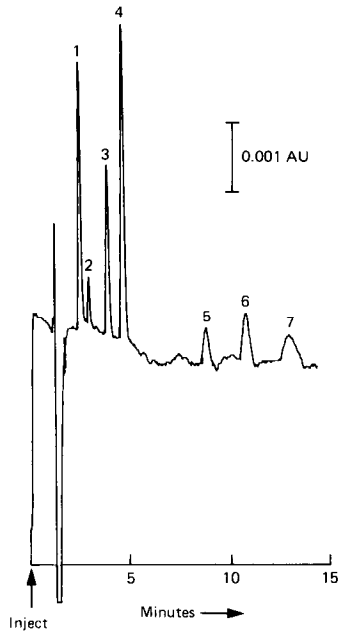

Fig. 6. Chromatogram of a sample containing 1 mg/l each of Se as selenite (1), chloride (2), S as sulphate (5), Se as selenate (6) and S as sulphite (7), 0.05 mg N/l nitrite (3) and nitrate (4). Conditions: eluent, 0.015 *M* phosphate (pH 4.8); wavelength, 190 nm; detector attenuation, 0.01 AU; flow-rate, 2 ml/min; sample volume, 100 μl.

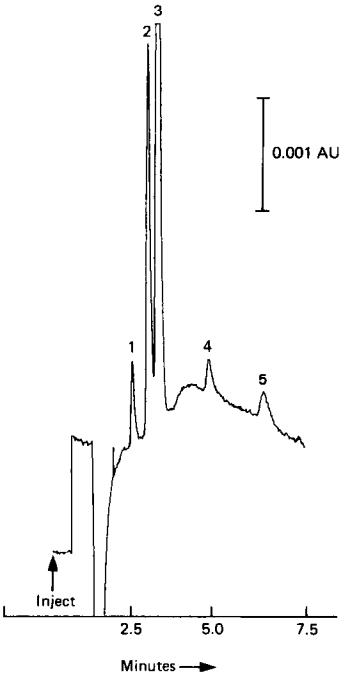

Fig. 7. Separation of 1 mg/l chloride (1) and S-sulphate (5), 0.1 mg N/l of nitrite (2) and nitrate (3), 0.1 mg/l iodide (4). Conditions as for Fig. 1, but pH 4.8 and attenuation 0.005 AU.

tigated. It was found that benzoate, phthalate, oxalate, citrate, tartrate as well as humic and fulvic acids were adsorbed very strongly within the pH range of 3–6. For this reason benzoate and phthalate are often used as marker ions[4,5] in ion chromatography.

The applicability of the method to water samples varying greatly in organic matter content and salinity was tested with organically polluted groundwater, seawater and tap water.

Results of applying the separation method to samples of groundwater taken from boreholes adjacent to a liquid waste disposal site are shown in Fig. 8A and B. In Fig. 8A one major peak at the start of the chromatogram can be seen and only traces ($\leqslant 10^{-6}$ *M*) in the carboxylic acid region. The major peak was not identified. Many organics elute in this region *e.g.* acetone, *n*-butanol, glycerol, phenol (Figs. 2 and 5). Urea and thio-urea also elute in this region and are detectable to 10^{-6} *M* at 190 nm.

Bromide (Fig. 8A and B) and iodide (Fig. 8B) are present in the groundwater at relatively high concentration (2.1 and 1.0 mg/l, respectively). In Fig. 9 results are shown (A) for a sample drawn from the water table under soil that had been sprayed with septage. From the chromatogram of the sample spiked with carboxylic acids (B) it is probable that acetate and/or propionate are present at a total concentration of about 5000 μM (peak 2). Acetate and propionate could not be resolved on the Vydac column. Peak 1 (Fig. 9) was not identified.

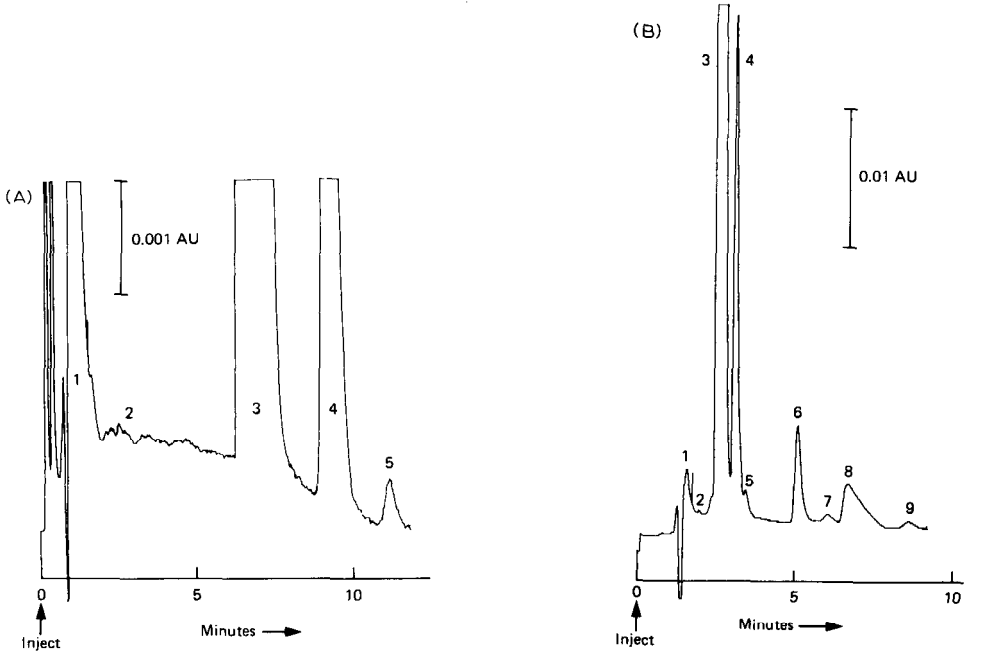

Fig. 8. (A) Chromatogram of a sample taken from a water table polluted by septage. Eluent, 0.01 *M* phosphate (pH 3.8); attenuation, 0.005 AU; other conditions as in Fig. 1. Peaks: 1 = unidentified; 2 = traces of organic acids (?); 3 = 290 mg/l chloride; 4 = 2.1 mg/l bromide; 5 = 0.012 mg N/l nitrate. (B) As for A, but 0.02 *M* phosphate (pH 4.6) as eluent and attenuation 0.04 AU.

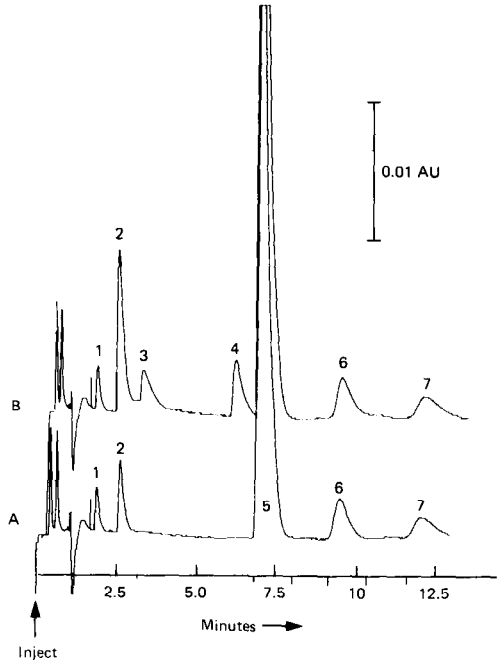

Fig. 9. Chromatograms of a sample of groundwater polluted by septage. The sample was diluted 1:10. Attenuation, 0.04 AU, other conditions as for Fig. 8A. Trace A: 1 = unidentified; 2 = acetate plus propionate (450 μM), 5 = 70 mg/l chloride; 6 = 0.54 mg/l bromide; 7 = 0.1 mg N/l nitrate. Trace B: 2, 3, 4 = 500 μM each of added acetate plus propionate (2), butyrate (3) and formate (4).

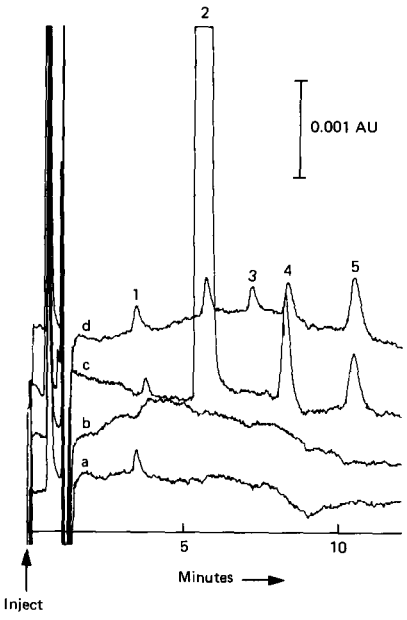

Fig. 10. Traces of bromide and nitrate in tapwater. Eluent, 0.02 M phosphate (pH 3.75); wavelength, 180 nm. Other conditions and peak numbering as in Fig. 8A. Traces; a = double quartz distilled demineralized water; b = double quartz distilled tap water; c = tap water; d = as a but spiked with 0.5 mg/l chloride (peak 2), 40 μg/l bromide (4), 20 μg N/l nitrite (3) and nitrate (5). Peak 1 was not identified.

In Fig. 10 a chromatogram of Perth (Wembley, Australia) tap water (3) is shown and compared with double distilled water prepared from deionized water (1) or tap water (2). Levels of chloride, bromide and N-nitrate (4) in the tap water were found to be 160, 0.13 and 0.02 mg/l, respectively.

Analyses of anions in the presence of high levels of chloride are easily accomplished. In Fig. 11A and B results are shown for bromide and sulphate in seawater diluted 1:10. The chloride, bromide and S-sulphate concentratuions were found to be 19 000, 70 and 750 mg/l, respectively. Above about 2000 mg/l chloride the resolution on the Vydac column was adversely affected.

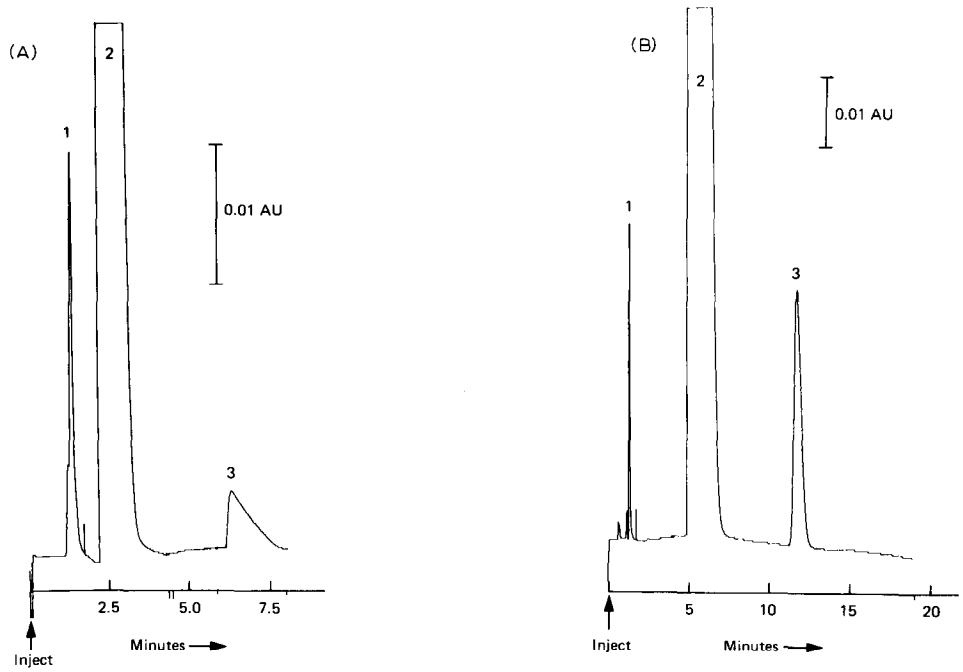

Fig. 11. (A) Chromatogram of seawater diluted 1:10. Conditions as for Fig. 8B, attenuation, 0.04 AU. Peaks: 1 = unidentified; 2 = chloride plus bromide; 3 = 75 mg S/l sulphate. (B) Chromatogram of seawater diluted 1:10. Eluent, 0.01 *M* phosphate (pH 3.6). Attenuation, 0.08 AU, other conditions as in Fig. 1. Peaks: 1 = unidentified; 2 = 1900 mg/l chloride; 3 = 7 mg/l bromide.

CONCLUSIONS

Single-column ion chromatography with UV detection below 195 nm has great potential for direct trace analysis of many organic and inorganic anions in surface and groundwater. Detection levels at the μg/l level or less should be attainable by improvement of the stability and energy output of UV sources below 195 nm and, if possible, concentrating the sample on a pre-column before injection.

When analysing anions that are easily oxidized special attention must be given to both sample preservation and catalytic effects of the HPLC materials in contact with the sample. Especially for iodide large losses occur when the concentration is less than 0.1 mg/l.

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