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ANION CHROMATOGRAPHY WITH LOW-CONDUCTIVITY ELUENTS. II.

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SUMMARY

Common inorganic anions can be separated on an anion-exchange column of low capacity using a very dilute solution of potassium benzoate or potassium phthalate as the eluent and a conductance detector. For each anion studied a plot of log adjusted retention time vs. log eluent concentration yields a linear plot. Elution data for additional anions are reported with various resins and eluents. Several new practical separations of anion mixtures are given. By decreasing the eluent concentration with a resin of very low capacity, the sensitivity of detection can be improved so that it becomes feasible to separate mixtures of anions in the low ppb** concentration range.

INTRODUCTION

Ion chromatography as developed by Small *et al.*¹ has allowed the rapid separation and quantitative determination of inorganic and organic anions. Their system, which is marketed as a commercial instrument by the Dionex Corporation (Sunnyvale, Calif., U.S.A.), uses a separation column containing a patented anion-exchange resin. The separated anions are detected by conductance after passing through a hydrogen-form cation-exchange column (called a suppressor column) to remove most of the background conductance of the eluent. In a previous paper we described a simple method called anion chromatography that separates mixtures of anions without a suppressor column². The absence of a suppressor column permits continuous operation of the system without any need for regeneration.

In the present work a larger number of anions have been studied and a linear correlation of log retention time with log of eluent concentration is noted. A selective method for separation of bicarbonate is described and several other examples of new separations are presented. Finally, it is shown that resin capacity and eluent concentration can be manipulated to significantly improve the sensitivity of anion chromatography.

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** Throughout this article, the American billion (10⁹) is meant.

EXPERIMENTAL

Sample solutions

Calibrated solutions of the potassium salts of various anions (fluoride, chloride, sulfate, etc., as shown in the chromatograms) were prepared from analytical-grade reagents.

Ion-exchange resins

Two kinds of ion exchangers served as the stationary phase of the analytical column, viz. the relatively high-capacity, commercially available Vydac SC (Separations Group, Hesperia, Calif., U.S.A.) anion-exchange resin (bead size: 30–44 μm , capacity: 0.1 mequiv./g), and a low-capacity anion-exchange resin prepared at this laboratory by the following method:

The copolymer used as starting material for the synthesis of the anion-exchange resins were Rohm and Haas (Philadelphia, Pa., U.S.A.) macroreticular cross-linked polystyrene beads XAD-1. This resin is highly cross-linked and has excellent chemical and mechanical stability. The beads were ground and sieved, fines removed and the fraction of 250–325 mesh was collected for the synthesis.

A 5-g portion of that fraction was swollen in a mixture of 10 ml chloromethylmethyl ether, 40 ml methylene chloride and 3 ml nitromethane. When 1.1 g of zinc chloride were added to the mixture the reaction was initiated and was maintained at room temperature for 5 min, after which the reaction was quenched by adding water to the mixture. The beads were then filtered, washed with water and methanol and finally air dried.

The chloromethylated beads were aminated by adding trimethylamine-methanol (25:75) and allowing the reaction to proceed overnight. The final product was washed with 1 *M* HCl, 2-propanol, and water, and was dried overnight at 60°. The capacity of the XAD-1 anion-exchange resin was determined by converting a weighed amount of resin to the nitrate form and analyzing the displaced chloride by anion chromatography. The capacity was found to be 0.007 mequiv./g.

Eluents

Potassium benzoate solutions were made up in concentrations varying $1.0 \cdot 10^{-3}$ to $1.0 \cdot 10^{-4}$ *M* and buffered to a pH of 6.25. Potassium phthalate solutions were prepared from potassium acid phthalate in concentrations ranging from $5.0 \cdot 10^{-4}$ to $5.0 \cdot 10^{-5}$ *M*; in general the solutions were buffered at pH 6.25, but for one study the pH was 4.50 and 6.75.

Apparatus

The chromatographic system was described in an earlier publication¹. It consists of pump, sample injection valve, resin column 500 \times 3 mm I.D., a conductance detector, and a recorder.

RESULTS

Comparison of eluents

In earlier work² resins of 0.07, 0.04, and 0.007 mequiv./g were used. Of these, the lowest capacity resin has been found to give sharper separations with improved

TABLE I

ADJUSTED RETENTION TIMES OF ANIONS USING MONOVALENT AND DIVALENT ELUENT ANIONS ON XAD-1, 0.007 mequiv./g

<i>Anion</i>	<i>Adj. retention time (min)</i> <i>benzoate (2.0 · 10⁻⁴ M,</i> <i>pH 6.25)</i>	<i>Adj. retention time (min)</i> <i>phthalate (1.0 · 10⁻⁴ M,</i> <i>pH 6.25)</i>	<i>Adj. retention time benzoate</i>
			<i>Adj. retention time phthalate</i>
F ⁻	2.28	1.40	1.63
Acetate ⁻	2.40	1.40 (neg)	1.71
Formate ⁻	2.34	1.50 (neg)	1.56
H ₂ PO ₄ ⁻	2.20	1.74 (neg)	1.26
HCO ₃ ⁻	2.22	1.80 (neg)	1.23
Cl ⁻	2.30	1.46	1.58
NO ₂ ⁻	2.90	1.60	1.81
Br ⁻	4.16	1.88	2.21
NO ₃ ⁻	3.74	1.90	1.97
I ⁻	8.14	2.92	2.79
SCN ⁻	12.8	5.54	2.31
ClO ₄ ⁻	22.8	6.96	3.26
SO ₄ ²⁻	∞	7.64	∞
SO ₃ ²⁻	∞	7.74	∞
C ₂ O ₄ ²⁻	∞	8.10	∞
CrO ₄ ²⁻	∞	5.20	∞
S ₂ O ₃ ²⁻	∞	12.9	∞

TABLE II

ADJUSTED RETENTION TIMES OF ANIONS USING MONOVALENT AND DIVALENT ELUENT ANIONS ON VYDAC SC RESIN

<i>Anion</i>	<i>Adj. retention time (min)</i> <i>benzoate (1.0 · 10⁻³ M,</i> <i>pH 6.25)</i>	<i>Adj. retention time (min)</i> <i>phthalate (5.0 · 10⁻⁴ M,</i> <i>pH 6.25)</i>	<i>Adj. retention time benzoate</i>
			<i>Adj. retention time phthalate</i>
F ⁻	?	?	—
Acetate ⁻	1.25	0	∞
Formate ⁻	1.90	0	∞
Cl ⁻	4.72	1.00	4.72
NO ₂ ⁻	8.00	1.96	4.08
Br ⁻	20.6	4.82	4.27
NO ₃ ⁻	28.5	7.34	3.88
SO ₄ ⁻	21.6	4.58	4.71
SO ₃ ²⁻		4.56	
Rest monovalent	∞	∞	
Rest divalent	∞	∞	

sensitivity. In Table I are listed the adjusted retention times for seventeen anions chromatographed on the 0.007 mequiv./g anion-exchange resin. The results confirm that phthalate is a more efficient eluent than benzoate because retention times with benzoate are longer than with phthalate even though the normality of the eluents is equal. In Table II the adjusted retention times for the two eluents are compared for chromatograms on Vydac resin. Again the adjusted retention times are longer with the benzoate eluent. Further comparison shows that retention times are longer on the Vydac resin than on the XAD-1 resin (0.007 mequiv./g) even though the

benzoate eluent concentration used with the Vydac resin is five times that used with the XAD-1 resin.

Adjusted retention times are compared in Table III for anions on a Vydac SC resin column for phthalate eluents of two different pH values. At the lower pH much of the eluent is in the hydrogen phthalate form, while at the higher pH value the divalent phthalate anion predominates. The results indicate that a much more rapid elution is obtained with eluent containing a divalent anion. The ratio of the adjusted retention times show that divalent analyte anions are more affected by an eluent pH change than are monovalent analyte anions. Of course, the pH of the eluent would also affect the form of the sample anions in some cases. For example, phosphate could be taken up either as $H_2PO_4^-$ or as HPO_4^{2-} , depending on pH. The more rapid elution of phosphate at pH 6.75 suggests that the effect of pH on the eluent is more important in this case than its effect on the form of the phosphate anion. The pH of an eluent may also affect background conductivity. The consequence of this is that phosphate appears as a negative peak when the higher conducting pH 6.75 eluent is used.

TABLE III
ADJUSTED RETENTION TIMES OF ANIONS FOR TWO DIFFERENT pH VALUES OF POTASSIUM PHTHALATE ON VYDAC SC RESIN

Anion	Adj. retention time (min) phthalate ($5.0 \cdot 10^{-4} M$)		Adj. retention time pH 4.50
	pH 4.50	pH 6.75	Adj. retention time pH 6.75
F ⁻	?	?	
Cl ⁻	1.70	1.12	1.52
NO ₂ ⁻	3.24	2.12	1.53
Br ⁻	7.12	4.88	1.46
NO ₃ ⁻	9.42	7.74	1.23
H ₂ PO ₄ ⁻	1.72	1.00 (neg)	1.72
SO ₄ ²⁻	24.4	4.48	5.45
SO ₃ ²⁻	24.5	4.46	5.49
Rest monovalent	∞	∞	
Rest divalent	∞	∞	

Effect of eluent concentration

The effect of eluent concentration on the adjusted retention time for an anion was determined by plotting log of adjusted retention time ($\log t'$) vs. \log [eluent]. The plots were straight lines as may be predicted by considering the equilibrium for anions exchanging on a strong base anion-exchanger:



where R represents the anion exchanger, and A and B are competing anions. K , the selectivity coefficient, is

$$K_B^A = \frac{[A-R_y]^y [B]'}{[A]'^y [B-R_x]^y} \quad (2)$$

In column chromatography the sample normally uses 1% or less of the resin capacity; therefore $[B-R_x]$ is essentially constant and equal to the resin capacity.

A column operation in which B is the eluent anion and A is a sample anion, the term $[B]^y$ may be written as $[\text{eluent}]^y$. The ratio of $[A-R_x]$ to $[A]$ is an A distribution ratio, D , which can be related to the adjusted retention time for the elution of A from the column. Substituting these into eqn. 2:

$$K_B^A = D^x \cdot \frac{[\text{eluent}]^y}{\text{capacity}^y} \quad (3)$$

D is related to the adjusted retention time, t' , by the equation

$$D = \frac{t'}{W} \quad (4)$$

where W is the weight of the resin in the column. Substituting this into eqn. 3:

$$K_B^A = \frac{t'^x}{W^x} \cdot \frac{[\text{eluent}]^y}{\text{capacity}^y}$$

Rearranging and taking the log of both sides:

$$\log K_B^A W^x = x \log t' + y \log [\text{eluent}] - y \log \text{capacity} \quad (5)$$

or

$$\log t' = \frac{-y}{x} \log [\text{eluent}] - \text{constant}$$

y is the charge of the sample anion and x is the charge of the eluent anion. The terms other than t' and $[\text{eluent}]$ are constant for each anion. The slope of $\log t'$ vs. $\log [\text{eluent}]$ plot will vary from 0.5 to 2 depending on the charge of the anions involved.

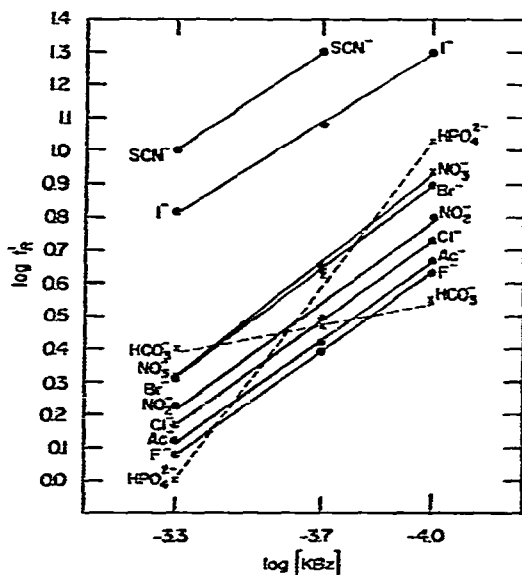


Fig. 1. Adjusted retention times of anions for different concentrations of potassium benzoate using XAD-1 0.007 mequiv./g.

Linear plots of $\log t'$ vs. \log eluent were obtained experimentally in all cases. Fig. 1 shows results for XAD-1 resin (0.007 mequiv./g) for varying concentrations of potassium benzoate eluent. Monovalent anions all have slopes less than the theoretical slope of -1 . Phosphate has a slope of approximately -2.1 , indicating that it is retained as the divalent anion. The slope of the bicarbonate is unusually low. The bicarbonate ion undoubtedly is in equilibrium with molecular carbonic acid, which may also be retained by the resin. The very low slope obtained makes it possible to adjust conditions so that bicarbonate is eluted before all other common anions.

In Fig. 2 the behavior of several anions is plotted as a function of benzoate concentration for Vydac SC resin. The slopes are even lower than with the XAD-1 resin in Fig. 1. There is a distinct difference between the adjusted retention times of formate and acetate, and also between these anions and chloride.

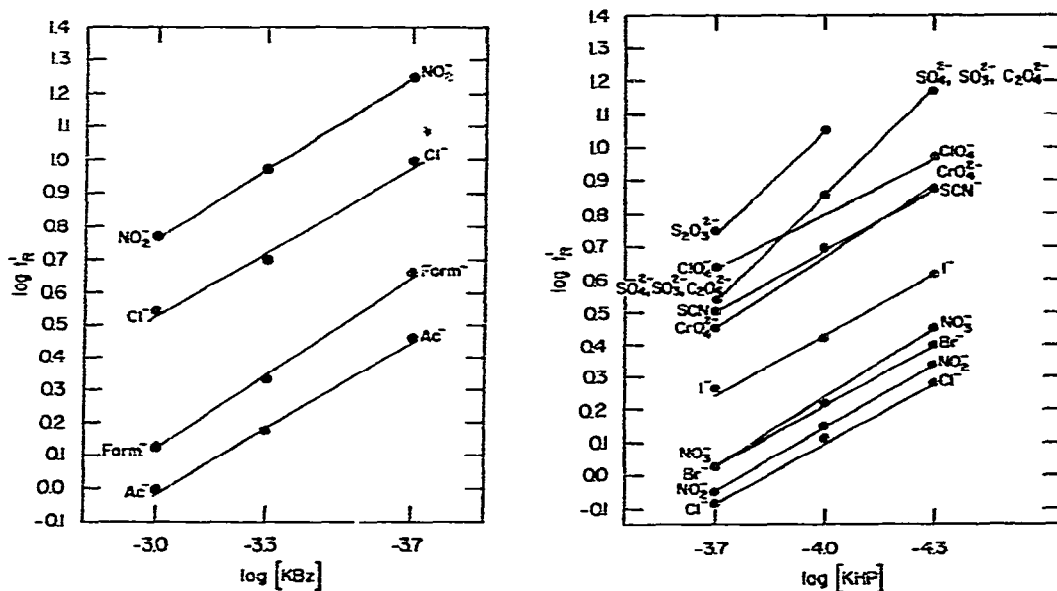


Fig. 2. Adjusted retention times of anions for different concentrations of potassium benzoate using Vydac SC anion-exchanger. Ac = Acetate; Form = formate.

Fig. 3. Adjusted retention times of anions for different concentrations of potassium phthalate using XAD-1 0.007 mequiv./g.

Adjusted retention times are plotted as a function of potassium phthalate concentration for XAD-1 resin (Fig. 3) and for Vydac SC resin (Fig. 4). Assuming the eluent anion is entirely present as phthalate (-2), the theoretical slope should be -1 for each divalent anion and -0.5 for each monovalent anion. In Fig. 3 the slopes for sulfate, sulfite and oxalate are very close to the theoretical, but the slopes of most of the monovalent anions are higher than predicted. The greater slope of the divalent anions with respect to the monovalent is very convenient. By adjusting the eluent concentration, elution of sulfate, sulfite or oxalate can be slowed down for better separation from monovalent anions, or elution can be speeded up for a more

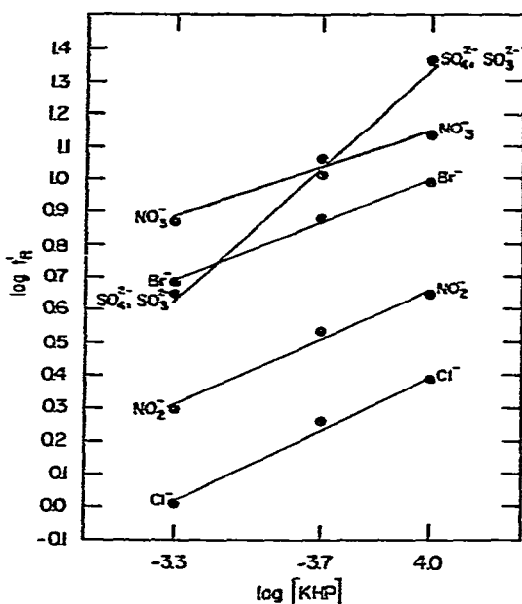


Fig. 4. Adjusted retention times of anions for different concentrations of potassium phthalate using Vydac SC anion-exchanger.

rapid determination of any of these divalent anions. The results with Vydac resin show a rather good agreement with the predicted slopes except for chloride.

New separations

By using approximately $1.0 \cdot 10^{-4}$ M benzoate as the eluent, bicarbonate is eluted before any of the other anions studied (see Fig. 1). Bicarbonate in a tap water sample was determined. Fig. 5 shows a small bicarbonate peak in a diluted tap water sample; the peak is larger after addition of some bicarbonate to the sample. Using several standard additions of bicarbonate, a linear plot, shown in Fig. 6, was obtained. Extrapolation of the plot indicated a bicarbonate concentration of 52 ppm in the original water sample. The optimum pH of the eluent is approximately 5.7. A pH of 6.25 works well but a higher pH would result in broadening of the bicarbonate peak. Even though the sample also contained a large amount of sulfate, this did not interfere with later injections. The sulfate is a late-eluting anion under these conditions, and will only be seen as a slight shift in the baseline.

In the same water sample chloride and sulfate were each determined by anion chromatography, calcium plus magnesium were determined by titration with EDTA, and sodium and potassium were measured by atomic spectroscopy. The following material balance was obtained: calcium plus magnesium, 2.96 mequiv./l; sodium plus potassium, 0.89 mequiv./l; total cations, 3.85 mequiv./l; sulfate, 1.87 mequiv./l; chloride, 1.02 mequiv./l; bicarbonate, 0.85 mequiv./l; total anions, 3.74 mequiv./l. The material balance is considered to be satisfactory in that some minor constituents (fluoride, for example) were not measured.

Phosphate has now been included in the list of anions that can be determined

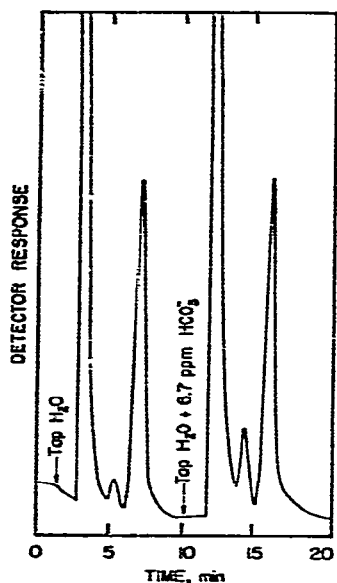


Fig. 5. Separation of total carbonate from all other anions in Iowa State University tap water using $1 \cdot 10^{-4} M$ potassium benzoate, pH 6.25, on XAD-1 0.007 mequiv./g.

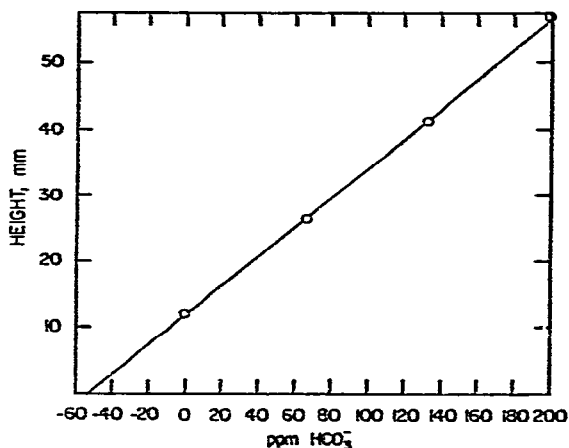


Fig. 6. Standard addition curve for determining bicarbonate in Iowa State University tap water.

successfully by anion chromatography. Fig. 7 shows the chromatogram of a leading cola drink, diluted with distilled water. The bicarbonate peak, resulting from carbon dioxide in the original sample, decreased as the sample stood and some carbon dioxide was lost. The carbon dioxide was at least partially converted to bicarbonate upon injection by the buffering action of the eluent. It seems likely that carbon dioxide in various aqueous samples can be determined quantitatively by first buffering the sample to convert the carbon dioxide to bicarbonate, then determining the bicarbonate by anion chromatography.

Fig. 7 shows that the initial phosphate peak increases in height when phosphate is added to the sample. Again using the standard addition method, a linear plot was obtained with an extrapolated intercept that indicated 610 ppm of HPO_4^{2-} in the original cola sample.

Formate and acetate are difficult to separate from each other by ion chromatography. Fig. 8 shows a good separation of these anions from each other and from chloride and nitrite on a column containing Vydac resin.

Increasing the sensitivity of separations

With phthalate eluent, it was observed that many anions could be eluted in a reasonable time even with eluents as dilute as $5.0 \cdot 10^{-5} M$ and lower provided a low-capacity resin was used. With such dilute eluents, many of the anion peaks at first were excessively broad and showed fronting. However, when the concentration of the sample anions was reduced, good peaks were again obtained.

The conductance of these eluents is lower than those used earlier ($1.0\text{--}5.0 \times 10^{-4} M$) and permits use of a more sensitive setting on the detector. Thus, by using a

low capacity resin and a more dilute eluent, anions can be successfully chromatographed at lower concentration levels. Fig. 9 shows two separations of a mixture containing four anions. By increasing the detector sensitivity setting, the concentrations of the anions can be decreased ten-fold and a good separation can still be obtained. Fig. 10 shows the chromatogram for separation of chloride, bromide and iodide at the ppb concentration level.

It will be seen that resin capacity and eluent concentration are powerful parameters that can be varied in tandem to increase the sensitivity of anion chromatography. Experiments are underway with resins of still lower capacity that may result in still lower detection limits.

DISCUSSION

If XAD-1 resin is assumed to be primarily polystyrene, it can be calculated that anion-exchange resin with a capacity of only 0.007 mequiv./g contains less than one quaternary ammonium functional group per 1000 benzene rings. This raises the question of whether the functional groups are distributed rather evenly throughout the resin or are clustered together near the more accessible surfaces. The latter case is suggested by the fact that phthalate, a -2 anion, is a more powerful eluent than benzoate, a -1 anion. Further support for this case is given by the difference in slopes of -1 and -2 anions in Fig. 3. These data suggest that sulfate, for example,

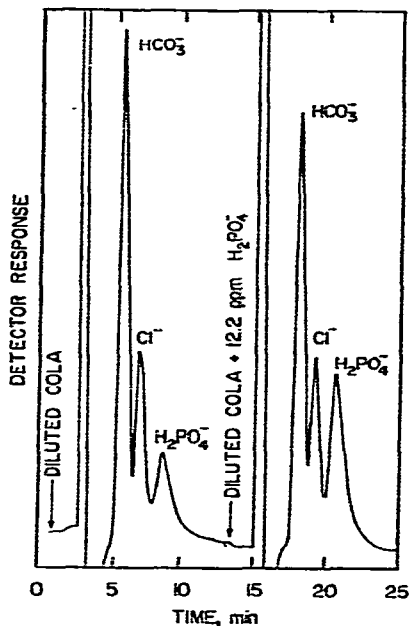


Fig. 7. Separation of phosphate from all other anions in a diluted cola drink using $1 \cdot 10^{-4}$ M potassium benzoate, pH 6.25, on XAD-1 0.007 mequiv./g.

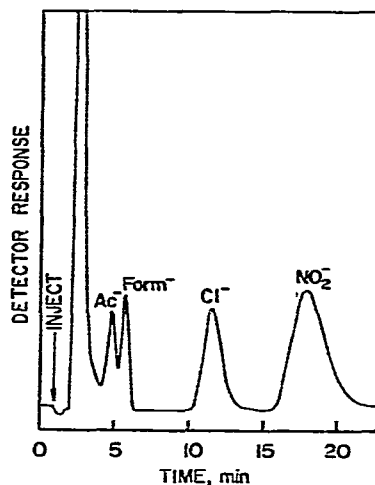


Fig. 8. Separation of 27.1 ppm acetate, 6.8 ppm formate, 5.1 ppm chloride and 15.8 ppm nitrite using $5 \cdot 10^{-4}$ M potassium benzoate, pH 6.25, on Vydac SC anion-exchange resin.

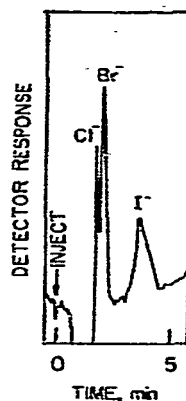
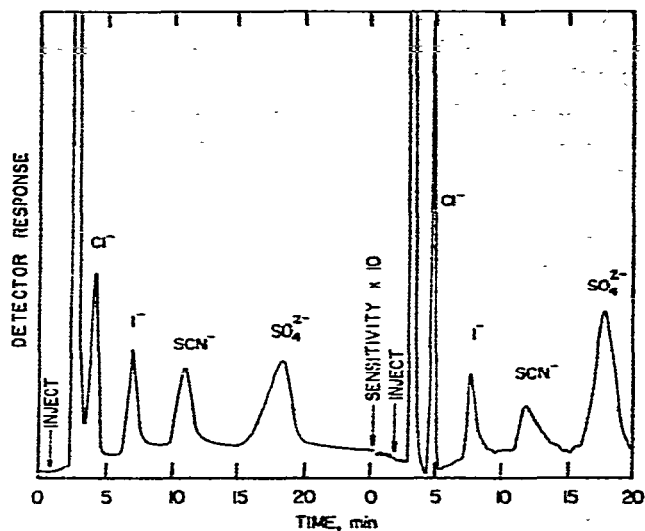


Fig. 9. Separation of 7.7 ppm chloride, 29.5 ppm iodide, 28.5 ppm thiocyanate and 16.5 ppm sulfate and the same mixture diluted by a factor of 10 using $5 \cdot 10^{-5} M$ potassium phthalate, pH 6.25, on XAD-1 0.007 mequiv./g.

Fig. 10. Separation of 20 ppb chloride, 65 ppb bromide and 98 ppb iodide using $5 \cdot 10^{-5} M$ potassium phthalate, pH 6.25, on XAD-1 0.007 mequiv./g.

behaves as a -2 anion and that each sulfate is associated in some way with two quaternary ammonium groups. The possibility that sulfate is associated with less than two resin functional groups and that electroneutrality is maintained by uptake of a positive counter ion was rejected after equilibrating a solution of potassium sulfate with some resin. Subsequent analysis showed no uptake of potassium by the resin.

Although columns containing Vydac resin give very good separations in many cases, we found a slow degradation of this resin which gradually shortens elution times for the various anions. In one case this gradual degradation caused sulfate to run into the bromide peak, although a good separation of the two had been obtained earlier with fresh resin. It was also observed that no fluoride peak can be obtained using Vydac resin.

The order of elution of anions (see Table I) is similar to that reported for conventional anion-exchange resins and also is consistent with the hydration energies and polarizabilities. On XAD resins of very low capacity fluoride and chloride prefer the dilute aqueous phase over the resin, and are poorly resolved. Bromide and iodide, with their smaller hydration energies and higher polarizabilities, elute much later and are well resolved. Nitrite is somewhat displaced in the order of elution. It should elute before chloride if hydration and polarizability were the sole consideration, but nitrite is a polyatomic ion stabilized by resonance structures and cannot be directly compared with halide ions. Thiocyanate elutes still later, after iodide, because of its lower hydration energy and higher polarizability.

ACKNOWLEDGEMENT

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