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DETERMINATION OF TRACES OF INORGANIC ANIONS BY MEANS OF HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY ON ZIPAX-SAX COLUMNS

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SUMMARY

Zipax-SAX pellicular beads are used as the anion-exchanger material; a high-pressure packing technique is described. A Zipax-SAX column (200 × 4.5 mm) is used in a separation system with eluent suppression and conductivity detection as in ion-chromatography. Good separation of chloride, nitrite, bromide, nitrate and sulfate is obtained with 1.4×10^{-3} M succinate or adipate eluents at pH 7. A complete separation takes about 6 min at a flow rate of 3 ml min^{-1}. Detection limits of 2 $\mu g\ l^{-1}$ chloride, 4 $\mu g\ l^{-1}$ nitrate and 10 $\mu g\ l^{-1}$ sulfate can be reached if 2 ml of sample is preconcentrated.

Ion-chromatography, initiated by Small et al. [1], has found widespread application in the field of environmental analyses [2, 3]. Well-packed analytical columns are essential to achieve high efficiency. Ideally, separation columns must be packed with small, rigid ion-exchanger beads at high pressure. In this paper, a packing procedure, for Zipax-SAX anion-exchange material will be described and some results obtained with this column will be presented.

The use of Zipax pellicular silica particles has some advantages. First, the thin layer (partly) surrounding the impervious silica core of the Zipax particles gives rise to a rapid radial mass transfer of the solute in the resin phase; consequently, the corresponding contribution to the plate height is small. Secondly, the particle diameter of Zipax is relatively small (25–37 μm), which means that the contribution of slow radial solute diffusion in the mobile phase to the plate height is limited. Thirdly, as the capacity (12 $\mu eq\ g^{-1}$ dry material) is low, fast separations can be achieved with relatively weak eluents. The main disadvantage seems to be that Zipax is only stable at pH 3—8 because of its silica core. Hence, carbonate solutions of sufficient strength cannot be applied as eluents. Therefore, some alternative eluents will be proposed which can be applied successfully at pH 7.

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EXPERIMENTAL

Chemicals

Zipax-SAX beads (particle diameter 25—37 μm; Du Pont de Nemours, Den Bosch, The Netherlands) are used in the separator column. According to the supplier, Zipax-SAX is a strong pellicular anion-exchanger with a capacity of about 12 μeq of quaternary ammonium groups per gram of dry material. The mean thickness of the resin (methacrylate) layer around the compact spherical silica core is 1.2 μm. Zipax-SAX cannot be applied in organic solvents and phosphate buffers, or at temperatures above 50°C.

The resin used in the suppressor columns is AG-50W-X12 (>400 mesh; Bio-Rad Laboratories), which is a strong cation-exchanger prepared from a styrene—divinylbenzene copolymer with 12% cross-linker. It has a capacity of 5 meq of SO_3H groups per gram of dry resin. Both ion-exchangers were used as received.

Adipate and succinate solutions were prepared by adjusting the corresponding acid solutions to the desired pH with sodium hydroxide.

Apparatus, column packing technique and measuring procedure

The scheme of the ion-chromatographic apparatus is given in Fig. 1. It is equipped with a reciprocating piston pump (Kipp-Analytica, Emmen, The Netherlands). The pulse dampener system consists of an Orlita (Giessen/Lahn, West Germany) pulse dampener and a stainless steel resistance capillary

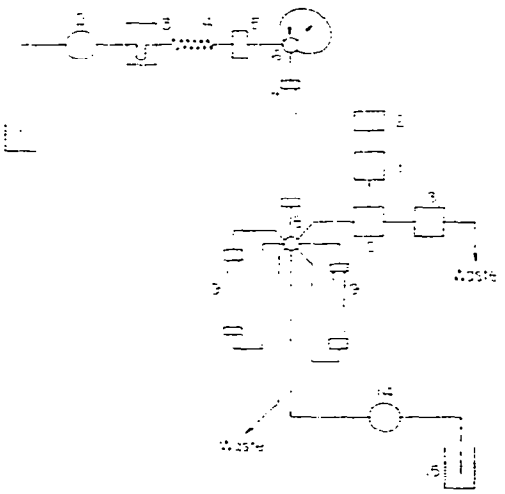

Fig. 1. Schematic diagram of the ion chromatograph. 1, Eluent reservoir; 2, pump; 3, pulse dampener; 4, capillary; 5, filter; 6, 6-port injection valve; 7, analytical column; 8, 8-port valve; 9, suppressor columns; 10, conductivity cell; 11, conductivity detector; 12, recorder; 13, siphon counter; 14, regeneration pump; 15, regeneration liquid (nitric acid or water).

(length 3 m, i.d. 0.25 mm). The stainless steel eluent filter (Chrompack, Middelburg, The Netherlands) has a pore diameter of 2 μm. The 6-port sample injection valve and the 8-port valve were supplied by Valco (Houston, TX). The former is equipped with a 50-μl sample loop. Both are actuated pneumatically. The home-made conductivity cell consists of two platinum electrodes in a perspex housing and has a cell volume of 6 μl. The digital conductivity detector has been described elsewhere [4]. The columns (precision-bore polished stainless steel, i.d. 4.5 mm) and the detector cell are surrounded by water jackets and thermostated by a Haake N_3B thermostat (Berlin, West Germany) to within 0.01°C. The connecting tubing (i.d. 0.25 mm) is kept as short as possible. Low dead volume connectors (see Fig. 2) are used, to minimize extra-column peak broadening. The eluent flow rate is monitored continuously with a calibrated siphon counter (home-made).

The column-packing apparatus is outlined in Fig. 3. The pump is of the reciprocating type and should attain a pressure of at least 400 bar when columns have to be packed with 10-μm particles. A Milton Roy pump (Chicago, IL) was used. Pulse dampening is achieved with a flow-through Bourdon gauge, a resistance capillary, an Orlita pulse dampener and another capillary in series. The stainless steel capillaries (length 3 m, i.d. 0.25 mm) ensure a nearly pulse-free flow. The slurry reservoir is a thick-walled stainless steel tube equipped with teflon-sealed stainless steel nuts. The lower nut is part of the polished precolumn (length 10 cm). The internal diameter of the pre-column, connector and column should be equal. The packed bed in the column is kept in place by means of a thin plug of wool in a low dead-volume connector.

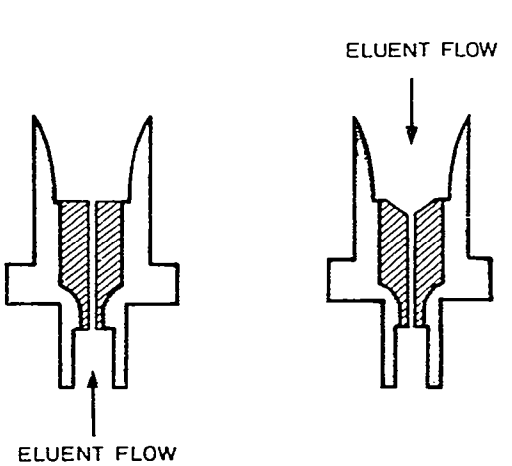

Fig. 2. Low dead-volume stainless steel inlet and outlet connector.

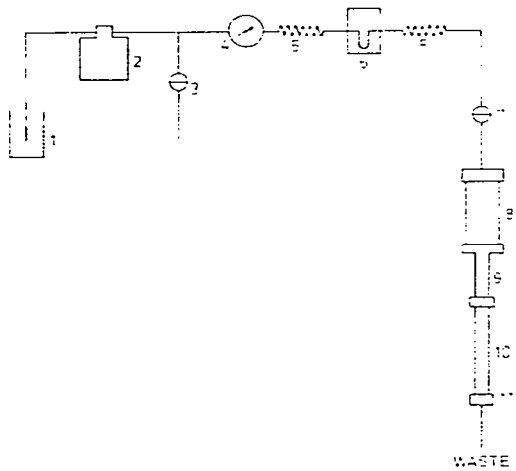

Fig. 3. Scheme of the column-packing apparatus. 1, Reservoir (methanol or water); 2, pump; 3, valve; 4, manometer; 5, capillary; 6, pulse dampener; 7, valve; 8, slurry reservoir; 9, precolumn; 10, column; 11, plug of wool in low dead-volume connector.

The columns are packed according to the viscous slurry method proposed by Asshauer and Halász [5]. The Zipax-SAX (5 g) is suspended in 25 ml of ethyleneglycol and 2.5 g of AG-50W-X12 in 25 ml of isopropanol. The slurries are degassed and homogenized by sonication. The column and precolumn are filled with tetrachloromethane in order to prevent inclusion of air bubbles in the packed bed. The slurry reservoir is filled with the slurry and thereafter methanol is added to remove all air up to the shut-off valve (7). When the pump and dampeners have been filled with methanol, the slurry reservoir is connected to the pump (with valve 7 closed). The apparatus is pressurized with methanol up to 400 bar. Thereafter, valve (7) is opened and the slurry is forced into the column. The packed bed is settled by flushing 200 ml of methanol and 200 ml of water through the column at maximum pressure.

Glass columns can also be slurry-packed by this method when the pressure across the column is kept below 60 bar. A short glass column (100 × 4.0 mm), packed with Zipax-SAX was used as a concentrator column.

The void volume of the separator column (V_m) is estimated from the retention volume of water. The capacity ratio k is calculated from the equation $k = (V_R - V_M)/V_m$, wherein V_R and V_M are the retention volumes of the solute and water, respectively, in the separator-suppressor column combination. The k values are independent of sample size (50—200 μl of solutions of 10 ppm nitrate and 10 ppm sulfate), only slightly dependent on the eluent flow rate (1.5—4.5 ml min^{-1}), and reproducible within 3%.

RESULTS AND DISCUSSION

Column efficiency and selectivity

The plate height is calculated from the chromatogram using the conventional equation $H = L\ (\sigma_t^2/t_R^2)$, wherein L is the column length, σ_t^2 is the variance of the peak and t_R is the retention time of the component. The linear velocity, v, is estimated from the eluent flow rate, F, using the equation $v = F/\pi r^2 \phi$, where r is the column radius and ϕ is the porosity of the column packing ($\phi \approx 0.4$ for a regular packing of compact spherical particles). Plate height data for nitrate and sulfate ions are given as a function of v in Table 1.

In order to discuss retention and selectivity on Zipax-SAX columns, it is convenient to relate the experimental capacity ratio data $k_{A,B}$ of ion A (trace constituent in eluent B) to the selectivity coefficient $K_{A,B}$. The ion-exchange equilibrium is given by

$$z_B\ A + z_A\ B_r \rightleftharpoons z_B\ A_r + z_A\ B \qquad (1)$$

wherein the index r refers to ions in the resin phase and z_A and z_B are the charges on ions A and B. The selectivity coefficient $K_{A,B}$ of this equilibrium is

$$K_{A,B} \equiv \{a_{A,r}/a_A\}^{z_B}\ \{a_B/a_{B,r}\}^{z_A} \simeq \{[A]_r/[A]\}^{z_B}\ \{[B]/a_{B,r}\}^{z_A} \qquad (2)$$

TABLE 1

Plate height data (H) for nitrate and sulfate ions as a function of the linear velocity (v) on a 200 × 4.0 mm Zipax-SAX column
(Eluent: 1.4×10^{-3} M sodium succinate, pH 7.)

v (cm s^{-1})	H (mm)	
	NO_3^- (k = 4.5)	SO_4^{2-} (k = 7.5)
0.50	0.31	0.31
0.78	0.35	0.36
1.03	0.39	0.41
1.53	0.44	0.47

where a and a_r denote activities. It is assumed that the concentrations of ion A in both phases and that of ion B in the eluent are small. Hence, $a_A \simeq [A]$, $a_{A,r} \simeq [A]_r$ and $a_B \simeq [B]$. Further, it is assumed that co-ions are excluded from the resin phase, which implies that in eqn. (2) $a_{B,r}$ is approximately constant. The capacity ratio $k_{A,B}$ is given by

$$\log k_{A,B} \equiv \log (n_{A,r}/n_A) = \log \{(W/V_m)([A]_r/[A])\} \quad (3)$$

In this equation $n_{A,r}$ and n_A are the numbers of moles of A in the resin and in the eluent, respectively; W is the weight of resin phase in the column. Combination of Eqns. (2) and (3) yields

$$\log k_{A,B} = \log (W/V_m) + (1/z_B) \log K_{A,B} - (z_A/z_B) \log ([B]/a_{B,r}) \quad (4)$$

Since the column parameters W, V_m, $a_{B,r}$ (related to the capacity of the ion-exchanger) and $K_{A,B}$ are constant at a given column temperature, Eqn. (4) can be simplified to

$$\log k_{A,B} = \text{constant} - (z_A/z_B) \log [B] \quad (5)$$

When the eluent ion B is only weakly absorbed, $K_{A,B}$ (and hence $k_{A,B}$) will be relatively large. This appears to be the case when monocarboxylate ions are used as eluent at pH 7. Even with concentrations up to 0.01 M of acetate, propionate, benzoate or hydrogencarbonate, mixtures of Cl^-, NO_2^-, Br^-, NO_3^- and SO_4^{2-} ions cannot be eluted within a reasonable time. Elution at higher eluent concentrations is accompanied by a reduction of the peak/noise ratio and will exhaust the suppressor column more rapidly. In contrast, tricarboxylate ions (like citrate) appear to be very strong eluents and can only be applied at concentrations (10^{-3} M at pH 7) where k values appear to depend on the ion composition and concentration of the sample (to avoid this complication very concentrated samples may be diluted).

For these reasons, monocarboxylate and tricarboxylate ions are not recommended as eluents on Zipax-SAX. Attention will be focused on the performance of dicarboxylate eluent ions. The suppressor column exchanges all cations in the eluent for protons. Hence, to obtain a low background conductivity in the eluent, the pK_{a1} values of the corresponding dicarboxylic

acids should be large. In this respect, oxalic acid (pK_{a1} = 1.23) is not suitable. But succinic acid (pK_{a1} = 4.16, pK_{a2} = 5.61) and adipic acid (pK_{a1} = 4.42, pK_{a2} = 5.41) appear to be quite useful. Optimal k values (ranging from 2 to 10) are obtained at pH 6—7 by adjusting the overall succinate or adipate concentration between 10^{-3} M and 2×10^{-3} M (Fig. 4). Log k values at pH 5, 6 and 7 are linearly related to log [$Succ^{2-}$] with z_A/z_B = 0.55 for monovalent ions and z_A/z_B = 1.15 for sulfate (see Eqn. 5). Hence, even at pH 5, where the dibasic succinate amounts to only 18% of the total succinate concentration, the divalent ions control the ion-exchange equilibrium (Fig. 4).

On Zipax-SAX the ions are eluted in the order $F^- < Cl^- < NO_2^- \approx H_2PO_4^- < Br^- < NO_3^- < SO_4^{2-}$. Fluoride is eluted together with the negative water peak. Typical chromatograms are shown in Fig. 5 at about the optimal conditions with respect to resolution and total time. On Zipax-SAX, the optimal eluent temperature for obtaining good resolution in the minimal time is about 25°C.

Calibration and detection limits

Calibration graphs for chloride, nitrate and sulfate were prepared for a 200 × 4.0 mm Zipax-SAX separator column with a 150 × 3.0 mm Bio-Rad AG-50W-X16 suppressor column and 1.4×10^{-3} M succinate or adipate solution as eluent. Conductivity peak heights were measured. In the 1.5—30 mg l^{-1} concentration range, 200-μl samples were injected, whereas at low

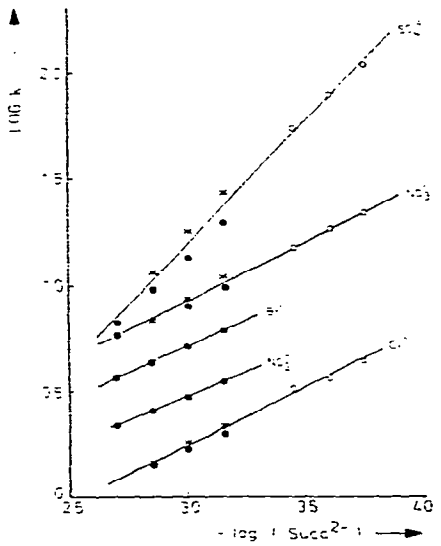

Fig. 4. Capacity ratio data (log k) for Cl^-, NO_2^-, Br^-, NO_3^- and SO_4^{2-} ions on a 200 × 4.5 mm Zipax-SAX column as a function of the dibasic succinate ion concentration in succinate solutions of different pH: (○) pH 5; (*) pH 6; (●) pH 7.

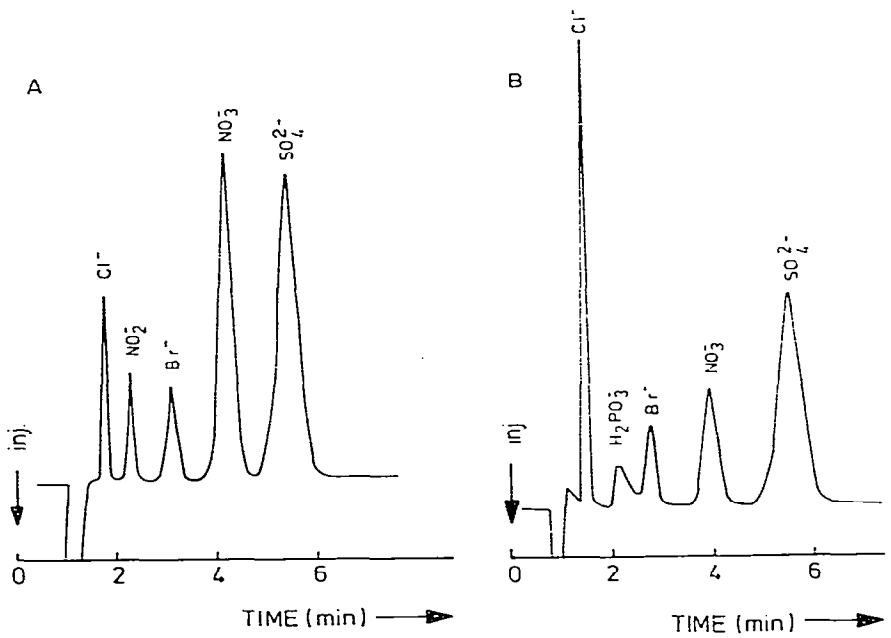

Fig. 5. Separation of trace anions on a 200 × 4.5 mm Zipax-SAX column. A, Separation of 2 mg l^{-1} Cl, 5 mg l^{-1} NO_2^-, 5 mg l^{-1} Br^-, 20 mg l^{-1} NO_3^- and 20 mg l^{-1} SO_4^{2-} with 2×10^{-3} M Na_2-adipate as eluent. B, Separation of 5 mg l^{-1} Cl^-, 5 mg l^{-1} $H_2PO_4^-$, 5 mg l^{-1} Br^-, 7.5 mg l^{-1} NO_3^- and 15 mg l^{-1} SO_4^{2-} with 1.4×10^{-3} M Na_2-succinate as eluent. Other conditions: pH 7, 50-μl loop, eluent flow rate 2.5 ml min^{-1}, 25°C.

concentrations (0.2—4 mg l^{-1}) about 2 ml of sample was preconcentrated in a 100 × 4.0 mm Zipax-SAX concentrator column, which was then switched into the eluent stream.

For the higher concentrations, the mean values of the peak height of four 200-μl injections and the peak height/concentration ratios are listed in Table 2 together with their relative standard deviations. The four calibration graphs were all made on the same day at intervals of about 4 h. Table 2 also shows the results for the low concentration samples, injected via a concentrator column. The peak heights are the mean values of three measurements. The calibration graphs were made at time intervals of one hour.

The results in Table 2 indicate that the calibration graphs for the higher concentration range are straight within experimental error. The same conclusion holds for sulfate in the lower concentration range, whereas for chloride and nitrate deviations from linearity are observed. Non-linear calibration graphs were also reported by Slanina et al. [6] for the calibration of nitrate in a 0.002 M Na_2CO_3/0.001 M $NaHCO_3$ eluent. Calibration graphs, based on peak heights in a system with eluent suppression and conductivity detection, are curved, in principle, and errors may be introduced (especially in the lower concentration range) if linear regression is applied. A detailed investigation of this effect is in progress. More accurate calibration is obtained

TABLE 2

Calibrations for chloride, nitrate and sulfate ions in the high concentration range with 1.4×10^{-3} M adipate as eluent and a 200-μl loop, and in the low concentration range with 1.4×10^{-3} M succinate as eluent and a concentrator column[a]

Standard (mg l^{-1})	Chloride			Nitrate			Sulfate		
	$\bar{S}$ (μmho)	$\bar{S}/c$ (μmho mg^{-1} l)	R.s.d. (%)	$\bar{S}$ (μmho)	$\bar{S}/c$ (μmho mg^{-1} l)	R.s.d. (%)	$\bar{S}$ (μmho)	$\bar{S}/c$ (μmho mg^{-1} l)	R. (%
High concentration range									
1.5	9.52	6.35	4	2.15	1.43	13	1.98	1.32	6
6	38.86	6.48	4	9.34	1.56	9	7.72	1.29	5
12	79.17	6.60	3	19.06	1.59	8	15.43	1.29	5
18	120.4	6.69	3	29.02	1.61	7	23.16	1.29	5
24	163.2	6.80	3	39.13	1.63	7	30.82	1.28	5
30	200.3	6.68	2	48.45	1.62	7	38.42	1.28	5
Low concentration range									
0.2	10.64	53.2	2.7	2.38	11.9	2.5	2.51	12.5	10
0.8	41.82	52.3	1.3	10.40	13.0	0.9	9.20	11.5	6
1.6	81.89	51.2	0.7	21.28	13.3	0.4	18.23	11.4	6
2.4	117.7	49.0	0.7	32.09	13.4	0.3	27.21	11.3	6
3.2	152.3	47.6	1.4	43.15	13.5	0.8	36.53	11.4	6
4.0	183.5	45.9	0.6	54.29	13.6	1.0	45.86	11.5	6

[a] c is the concentration of standard, $\bar{S}$ is the mean peak height and r.s.d. is the relative standard deviation (of $\bar{S}$ and $\bar{S}/c$).

with a curve-fitting procedure. Table 3 lists the results for four 200-μl samples. The mean values found, together with the relative standard deviations are given. These relative standard deviations are a measure of short-term reproducibility. The deviations of the concentrations found and injected (and the relative standard deviations in Table 2) are a measure of long-term reproducibility. Table 4 lists some results for the 2-ml samples that were injected via a preconcentrator column. The estimates of the long-term reproducibility from Tables 2 (low concentration range) and 4 (time interval between measurements ca. 1 h) are not significantly worse than the estimates of the short-

TABLE 3

Results obtained for chloride, nitrate and sulfate standards, injected via a 200-μl loop[a]

Concentration injected (mg l^{-1})	Concentration found (mg l^{-1})					
	Chloride		Nitrate		Sulfate	
	$\bar{x}$	R.s.d. (%)	$\bar{x}$	R.s.d. (%)	$\bar{x}$	R.s.d. (%)
1	0.96	1.0	1.00	2.0	1.01	1.0
5	5.01	0.6	5.00	0.2	4.95	0.2
10	9.98	0.7	10.18	0.3	10.08	0.5
20	20.08	0.3	19.98	0.3	20.14	0.3

[a] $\bar{x}$ is the mean value found and r.s.d. the standard deviation of the mean value. Ten determinations were made for each standard.

TABLE 4

Results obtained for chloride, nitrate and sulfate standards, injected via a concentrator column[a]

Concentration of ion injected ($\mu g\ l^{-1}$)	Concentration found ($\mu g\ l^{-1}$)					
	Chloride		Nitrate		Sulfate	
	$\bar{x}$	R.s.d. (%)	$\bar{x}$	R.s.d. (%)	$\bar{x}$	R.s.d. (%)
50	41.4	5.2	49.5	2.4	54.1	8.2
100	87.6	4.2	97.5	6.4	98.4	3.7
500	454	0.9	476	0.9	464	1.2
1000	929	1.4	964	1.0	938	1.6
2000	1872	0.8	1905	0.6	1863	1.2

[a] Abbreviations as in Table 3.

term reproducibility. The reproducibility of measurements of the high concentrations at time intervals of ca. 4 h (Table 2) is much worse, however. The deviations of the concentrations found and injected (in Table 4) are rather large and are probably the result of fluctuations in sensitivity, caused by changes in temperature and eluent flow rate.

Detection limits (three times the background noise) for chloride, nitrate and sulfate were determined for a 200-μl loop and for a concentrator column. They are given in Table 5.

The lifetime of a Zipax-SAX slurry packed separator column is at least 400 h. Deterioration of the packing resulting in peak broadening did not appear and almost no reduction of capacity was observed during that period. The lifetime of the suppressor column is at least three months.

Conclusions

Pellicular ion-exchangers with a silica core are well suited for the ion-chromatography of anions. In view of the instability of the silica core at high pH the traditional carbonate/hydrogencarbonate eluent must be replaced by a succinate/hydrogensuccinate or adipate/hydrogenadipate eluent. With these eluents, no deterioration of the column was observed over 400 hours

TABLE 5

Detection limits of chloride, nitrate and sulfate on the Zipax-SAX column with 1.4×10^{-3} M Na_2-succinate as eluent

Ion	Detection limit ($\mu g\ l^{-1}$)	
	200-μl loop	Concentrator column
Chloride	10	2
Nitrate	30	4
Sulfate	30	10

of use. Chloride, nitrite or phosphate, bromide, nitrate and sulfate are well separated within 6 min. With 25—37-μm particles, plate heights of 0.3 mm can be achieved for nitrate and sulfate ions. Detection limits are about 20 $\mu g\ l^{-1}$ for 200-μl samples, and about 5 $\mu g\ l^{-1}$ when 2-ml samples are preconcentrated.

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