



ELSEVIER

Journal of Chromatography A, 855 (1999) 91–109

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Application of experimental design for the characterisation of a novel elution system for high-capacity anion chromatography with suppressed conductivity detection

Michael Nowak^a, Andreas Seubert^{a,b,*}

^aUniversity of Hannover, Institute of Inorganic Chemistry, Callinstrasse 9, D-30167 Hannover, Germany

^bUniversity of Kassel, FB 19 Biology and Chemistry, Heinrich-Plett-Strasse 40, D-34132 Kassel, Germany

Received 14 January 1999; received in revised form 4 May 1999; accepted 31 May 1999

Abstract

A novel elution system for the application of high-capacity anion exchangers with suppressed conductivity detection in ion chromatography is presented. The ternary elution system is based on perchloric acid, sodium hydroxide and sodium carbonate. The novel elution system was applied to a self-made high-capacity anion-exchange column ($Q=453 \mu\text{equiv. Cl}^-$). A central composite design with 20 experiments was used to investigate the influence of the eluent compounds, which varied from 0.2 to 1.0 mM HClO_4 , 20 to 100 mM NaOH and 0 to 20 mM Na_2CO_3 , on the retention factor k' of seven common anions. A quadratic model including interactions was postulated. The model equations were used to estimate retention factors at known eluent compositions. No significant differences of calculated and experimental retention factors were found. Further statistical analysis was done by analysis of variance. The results showed that the three eluent compounds have completely different effects on the retention behaviour of the anions investigated. The elution of soft and weakly hydrated anions like bromide and nitrate is strongly influenced by the content of perchloric acid, whereas strongly hydrated anions like fluoride and sulphate are mainly affected by the hydroxide or carbonate content of the eluent. The results can qualitatively be explained comparing the relation of ionic radii to charge for eluent and analyte anions. As a consequence, the retention of the anions investigated can easily be manipulated by varying the contents of the eluent compounds. The usefulness of the novel elution system and high-capacity anion chromatography is demonstrated by the determination of trace anions in phosphate and fluoride matrices. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Experimental design; Mobile phase composition; Detection, LC; Suppressed conductivity detection; Retention factors; Anion exchangers

1. Introduction

Until now, the application of low-capacity ion exchangers dominates most separations in anion chromatography, mainly caused by the widespread use of conductivity detection as the most universal detection technique in ion chromatography. For direct conductivity detection, eluents must have a

*Corresponding author. Corresponding address: University of Hannover, Institute of Inorganic Chemistry, Callinstrasse 9, D-30167 Hannover, Germany. Tel.: +49-511-7623-174; fax: +49-511-7622-923.

E-mail addresses: nowak@mbox.acc.uni-hannover.de (M. Nowak), seubert@hrz.uni-kassel.de (A. Seubert)

low background conductance in order to enable satisfying sensitivity [1]. Therefore hydroxide- or carbonate-based eluents are used in combination with chemical suppression (suppressed conductivity detection). For non-suppressed conductivity detection, aromatic acids like phthalic or benzoic acid as well as inorganic buffers are utilised [2,3].

Low-capacity anion exchangers encounter problems when trace anions have to be determined in samples with high matrix contents. This may be the case in speciation analysis, quality control of high purity chemicals or the monitoring of water disinfection by-products where analyte ion concentrations are four- to five-orders of magnitude lower than matrix ion concentrations. If the matrix ion cannot be eliminated or reduced, it will in most cases strongly interfere the separation process resulting in a significant loss of separation efficiency due to column overload or peak overlapping.

Because of their higher content of functional groups, high-capacity anion exchangers can enable the analysis of samples of high ionic strength without matrix elimination steps. In addition, the use of large injection volumes or concentrated samples is possible. The usefulness of high-capacity anion exchangers has been demonstrated in several applications, e.g., the determination of bromate in disinfected water samples [4–6], the determination of anions in concentrated hydrofluoric acid [7] or the determination of nitrite and nitrate in water [8].

Despite the possibilities offered by high-capacity anion-exchange columns the number of publications is very small for two main reasons. First, high-capacity anion-exchange columns with satisfying chromatographic efficiencies are not commercially available. Today, the highest capacities available for anion chromatography are up to 180 $\mu\text{equiv.}$ per column [9]. Therefore either self-preparation [4–8] or the application of commercial high-capacity exchangers with poor chromatographic efficiency is necessary [10]. The second reason is the lack of an elution system suitable for conductivity detection. Even at elevated concentrations, common eluents for suppressed/non-suppressed conductivity detection are much too weak to elute anion-exchange columns with capacities above 200 $\mu\text{equiv.}$ per column. But higher eluent concentrations lead to a higher background conductance lowering the sensitivity of de-

tection. Until now, high-capacity anion chromatography has been possible only with detection modes that are not that much limited by the elution system, e.g., spectrophotometric, fluorimetric or amperometric detection [3].

Our aim was to establish an elution system suitable for high-capacity anion-exchange chromatography with suppressed conductivity detection. When continuously working membrane-suppressors are used, the upper concentration limits are about 100 mM for hydroxide and 20 mM for carbonate eluents. Further increase of eluent concentrations leads to incomplete suppression and unstable baselines.

The idea was then to modify the standard elution systems for low-capacity columns and suppressed conductivity detection. This was done by addition of perchlorate to the eluent. With spectrophotometric detection techniques, perchlorate has been an effective driving ion for the elution of high-capacity anion exchangers because of its high affinity to quarternary ammonia functional groups [4,6,7,11,12]. The result is a ternary elution system based on perchlorate, hydroxide and carbonate. Perchlorate cannot be chemically suppressed by an anion-suppressor. Therefore the maximum perchlorate content of the ternary elution system should not exceed 1 mM corresponding to a background conductivity of about 380 $\mu\text{S/cm}$. As discussed above, the upper concentration limits are 100 mM for hydroxide and 20 mM for carbonate.

The novel ternary elution system offers the possibility to vary the contents of three eluent compounds in order to manipulate the retention behaviour of the analytes. Applying an anion-exchange column with a capacity of 450 $\mu\text{equiv.}$, the concentrations of the eluent compounds may be varied from 0.2 to 1.0 mM HClO_4 , 20 to 100 mM NaOH and 0 to 20 mM Na_2CO_3 .

To investigate the influence of the eluent compounds on the retention of the so-called standard anions (fluoride, chloride, nitrite, bromide, nitrate, sulphate and phosphate), a statistical approach has been used. The application of an experimental design and statistical analysis of data provides high quality information about the retention behaviour of the analytes investigated by performing a rather small number of experiments [13–15]. By mathematically

fitting the measured data, model equations enable to estimate retention factors or selectivities at any eluent composition within the concentration range investigated. Furthermore, the effect of the eluent compounds on the retention of the analytes can accurately be quantified and the recognition of interactions between eluent compounds is possible.

2. Experimental

2.1. Basic substrate and modification

For preparing the high-capacity anion-exchange material, a custom-made polystyrene–divinylbenzene copolymer (PS–DVB) was used [16]. The resin had a degree of crosslinking of about 65% DVB with an average particle size of 6 μm . The surface area of the unmodified resin was about 580 m^2/g .

For the modification of the PS–DVB copolymer, the bromoalkylation method first introduced by Tomoi et al. was used [17]. This one-pot synthesis was originally intended for the preparation of polymer-supported spacer-modified phase-transfer catalysts. The synthesis involves ω -bromoalkenes as alkylating agents and trifluoromethanesulphonic acid (Triflic acid) as Lewis catalyst. In a second step, the alkylated polymer is treated with a tertiary amine to give a strong-basic anion exchanger. The principle

reaction scheme for the preparation of the packing material used in this study is shown in Fig. 1. 5-bromo-1-pentene was chosen for alkylation and 2-(dimethylamino)-ethanol for amination of the alkylated substrate.

2.2. Synthesis procedure

In an argon atmosphere, 15 g PS–DVB copolymer were suspended in 80 ml dry 1,2-dichloropropane at 20°C in a pre-dried 500-ml flask. After stirring for 10 min, 9.5 g (0.062 mol) trifluoromethanesulphonic acid was added. The reaction mixture immediately turned dark cherry red. A solution of 25 ml 5-bromo-1-pentene (0.205 mol) in 25 ml 1,2-dichloropropane was added dropwise to the mixture during a 45-min period. After the addition was complete, the reaction mixture was stirred for 48 h at 50°C under argon. The mixture was then cooled to 10°C, filtered and washed with 400 ml tetrahydrofuran (THF) and 200 ml 2 M HCl, deionised water, 2-propanol, methanol and finally acetone. The yield of functionalised polymer was 17.56 g.

The bromoalkylated resin was aminated for 24 h under reflux conditions using a mixture of 125 ml 2-(dimethylamino)-ethanol and 125 ml ethanol. The resin was filtered and washed with 200 ml 2 M HCl, deionised water, 2-propanol, methanol and acetone. The aminated polymer was dried at 50°C.

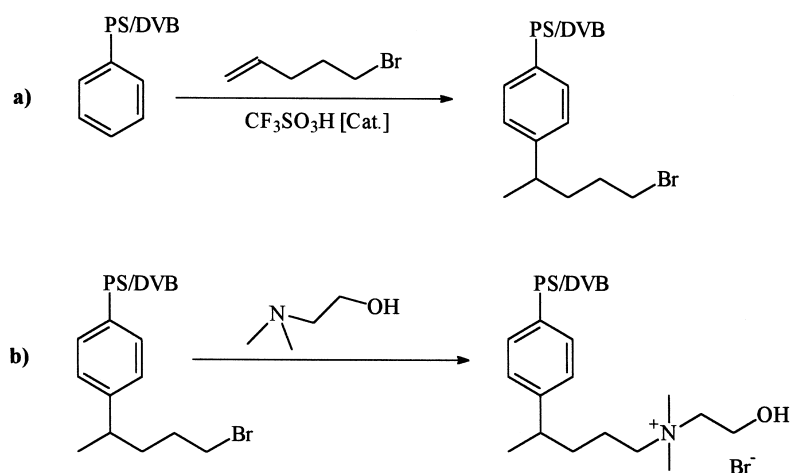


Fig. 1. Reaction scheme for the synthesis of the high-capacity anion exchanger: (a) Friedel–Crafts alkylation with 5-bromo-1-pentene; (b) amination with 2-(dimethylamino)-ethanol.

2.3. Instrumentation and chromatographic conditions

The high-performance liquid chromatography (HPLC) system consisted of the IC Pump 709, the Separation Center 733 which is equipped with a six-port stainless steel injection valve and the conductivity detector 732 (all Metrohm, Herisau, Switzerland). For chemical suppression of the eluent, the Anion-Self-Regenerating-Neutraliser ASRN I (Dionex, Idstein, Germany) was used in an external mode with 0.025 M H₂SO₄. All tubings, fittings and column housings (125×4 mm I.D.) were made of polyether ether ketone (PEEK). The eluent flow-rate was 1 ml/min in all cases. The injection volume was 300 µl. All investigations were carried out using analyte concentrations of 10 mg/l. Other chromatographic conditions are as noted in the figure captions.

2.4. Reagents

Trifluoromethanesulphonic acid and 5-bromo-1-pentene were obtained from Riedel-de Haën (Seelze, Germany). 2-(Dimethylamino)-ethanol and all solvents were from Fluka (Buchs, Switzerland) with a purity grade of at least 99% and were used as received.

All reagents for chromatographic investigations were of analytical grade (Merck, Darmstadt, Germany). Working standards were made by diluting stock solutions of sodium salts (1000 mg/l) with deionised water (Milli-Q, Eschborn, Germany). Aliquots of stock solutions of perchloric acid (0.5 M), sodium hydroxide (4 M) and sodium carbonate (1 M) were used to prepare eluents. The concentrations of NaOH were corrected for each eluent composition in order to neutralise the amount of perchloric acid used. Eluents were titrated with 0.025 M H₂SO₄ to verify the hydroxide and carbonate contents. The resulting eluent concentrations varied from 0.2 to 1.0 mM HClO₄, 20 to 100 mM NaOH and 0 to 20 mM Na₂CO₃ according to the experimental design.

2.5. Column packing and determination of exchange capacities

125×4 mm I.D. PEEK columns were packed

using a down-fill-slurry-technique. The functionalised polymer (ca. 1 g) was dispersed in 60 ml of a mixture of 100 ml glycerine and 42.5 g NaNO₃ diluted to 1000 ml with deionised water. The slurry was ultrasonically shaken for 15 min. It was immediately pressed into the column at a constant pressure of 25 MPa with a mixture consisting of 100 ml methanol and 68 g KH₂PO₄ diluted to 2000 ml with deionised water. At least 250 ml of this mixture was pumped through the columns. The back-pressure of the columns was about 8 MPa at a flow-rate of 1 ml/min.

To determine the strong-base capacities, the columns were rinsed with each 60 ml 0.2 M KCl and deionised water. The chloride was then eluted with 60 ml 0.2 M KNO₃ and quantified by potentiometric titration with 0.05 M AgNO₃. This procedure was repeated at least three times. The average column capacity was 450 µequiv. per column or 290 µequiv. per ml bed volume. The column used for this study had an exchange capacity of 453 µequiv. for chloride.

2.6. Statistics

2.6.1. Choice of experimental design

To study the effects of varying concentrations of eluent compounds on the retention behaviour of the so-called “standard-anions”, an experimental design technique was utilised. If k factors are involved, the simplest experimental design is a full factorial design (FFD) in which each factor can assume two levels (in coded units: ± 1) [14]. The number of experiments is then 2^k to explore all possible combinations. Considering $k=3$ factors, the experimental domain is a cube whose eight corner points represent the locations of the experiments. A full factorial design enables studying linear effects of variables and their interactions, but no statements can be made about second-order effects (curvature) because each factor has only two levels. The aim of this study is to describe the relationship between the concentration of eluent compounds c and the retention factor k' . The retention factor was calculated according to Eq. (1)

$$k' = (t_R - t_0)/t_0 \quad (1)$$

using the retention time t_R of each anion and the system dead volume t_0 which was determined by the retention time of the negative water dip at the beginning of each chromatogram. There is, following the common retention model for ion chromatography [3], an exponential dependence of k' on c . For practical use, as it is the case in this study, the retention factor may as well be fitted using a quadratic model.

An adequate model describing second-order effects must have at least three levels. In this case a central composite design (CCD) was used with three factors (eluent compounds) on five levels (concentrations of the eluent compounds) [13]. The CCD is build up of a full factorial 2^k design to which a star design is added. The length of the arms of the star determines the number of levels and the shape of the experimental design. The CCD is completed by addition of a center point. The principal representation of the CCD is shown in Fig. 2. The total number N of experiments with k factors is:

$$N = 2^k + 2k + c \quad (2)$$

The first term is related to the full factorial design, the second to the star points and the third to the center point. From the repetition of the center point, the experimental variance at the center of the domain can be estimated. For three factors to be considered, at least $8 + 6 + 1 = 15$ experiments are necessary.

The length of the arms of the star α plays a major

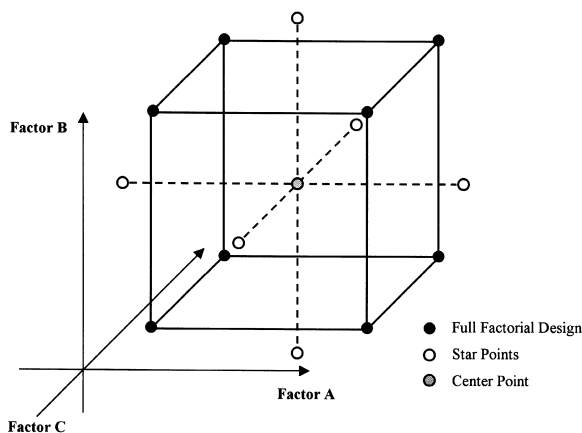


Fig. 2. Representation of a CCD with three factors on five levels. The length of the arm of the star is $\alpha=2$.

role for the appearance of the CCD. If $\alpha=1$, the star-points lie on the faces of the cube and the experimental domain is the same as defined by a 2^k full factorial design. Each variable assumes three levels $(-1/0/+1)$. If $\alpha \neq 1$, each variable will assume five levels $(-\alpha/-1/0/+1/+ \alpha)$. In this investigation, a CCD with $\alpha=2$ was chosen with a six-fold repetition of the center point ($c=6$) [18], as shown in Table 1. The value of $\alpha=2$ allows the levels of the three factors (concentration of eluent compounds) to be set equally spaced. The six replicates of the center-point allow an accurate evaluation of the experimental error, so that the significance of effects can be estimated. Note that the run-order of the experiments as shown in Table 2 must be randomised, which is the basic requirement for obtaining statistically independent responses and the correct determination of effects [13].

2.6.2. Statistical calculations

The response of the experiments was the retention factor k' of the anions investigated. The retention factors were fitted by a so-called response surface regression (RSR) including second-order and interaction terms. When k' is the response and the factors are A, B and C, the model equation would be the following:

$$k' = y + x_A A + x_B B + x_C C + x_{AA} A^2 + x_{BB} B^2 + x_{CC} C^2 + x_{AB} AB + x_{AC} AC + x_{BC} BC \quad (3)$$

The equation describes a four-dimensional surface. If one factor is kept constant at a medium level ("0" in coded units), the retention factor may be visualised in dependence on the other two variables in a three-dimensional response surface (RS).

The contribution of linear, quadratic and interaction terms to the regression polynomials was calculated by an analysis of variance (ANOVA) followed by an ϵ^2 -test [19]. The ANOVA shows the variances s^2 of different sources (e.g., linear or quadratic terms, residual error) and their significance as parts of the total variance. The ϵ^2 -test is a statistical method to determine the practical significance of an effect and demonstrates the extent of variability caused by the input to be investigated. ϵ^2 is calculated as follows:

$$\epsilon^2 (\%) = s_{(\text{Source})}^2 / s_{(\text{Total})}^2 \cdot 100\% \quad (4)$$

Table 1

Experimental matrix of the central composite design used for the investigation of the novel elution system (the values in parentheses indicate the coded levels of the factors which were used for data analysis and statistical calculations. The run-order is not randomised)

Experiment No.	$c(\text{HClO}_4)$ (mM) Factor A	$c(\text{NaOH})$ (mM) Factor B	$c(\text{Na}_2\text{CO}_3)$ (mM) Factor C
1	0.4 (−1)	40 (−1)	5 (−1)
2	0.8 (+1)	40 (−1)	5 (−1)
3	0.4 (−1)	80 (+1)	5 (−1)
4	0.8 (+1)	80 (+1)	5 (−1)
5	0.4 (−1)	40 (−1)	15 (+1)
6	0.8 (+1)	40 (−1)	15 (+1)
7	0.4 (−1)	80 (+1)	15 (+1)
8	0.8 (+1)	80 (+1)	15 (+1)
9	0.2 (−2)	60 (0)	10 (0)
10	1.0 (+2)	60 (0)	10 (0)
11	0.6 (0)	20 (−2)	10 (0)
12	0.6 (0)	100 (+2)	10 (0)
13	0.6 (0)	60 (0)	0 (−2)
14	0.6 (0)	60 (0)	20 (+2)
15	0.6 (0)	60 (0)	10 (0)
16	0.6 (0)	60 (0)	10 (0)
17	0.6 (0)	60 (0)	10 (0)
18	0.6 (0)	60 (0)	10 (0)
19	0.6 (0)	60 (0)	10 (0)
20	0.6 (0)	60 (0)	10 (0)

In a similar way the influence of the main factors (concentration of eluent compounds) on the retention factor was estimated. This was done by a one-way ANOVA, which represents the contribution of variance of a main factor (e.g., the content of perchloric acid in the eluent) to the total variance, again followed by an ϵ^2 -test.

Basic statistical calculations (regression, ANOVA) were carried out using the MINITAB software package, Release 12 (Minitab, State College, USA). Through-

out all calculations, the level of significance was $P \geq 95\%$ corresponding to a type I error of $\alpha \leq 0.05$. All further calculations were done with a spreadsheet program.

3. Results and discussion

3.1. Modification of the basic substrate

Considering chromatographic efficiency, spacer-modified PS–DVB copolymers for low-capacity anion chromatography were found to be superior to chloromethylated resins [20,21]. Therefore the bromoalkylation route proposed by Tomoi et al. was chosen for the preparation of a suitable high-capacity anion-exchange resin [17]. 5-Bromo-1-pentene reacted as alkylation reagent, resulting in a (1-methyl)-butylene chain between the polymer backbone and the functional group, in this case 2-(dimethylamino)-ethanol (Fig. 1). Although this alkylating reaction is less reactive than chloromethylation, especially when applied to copolymers with a high

Table 2

Average theoretical plate numbers per meter for the high-capacity anion-exchange column at the center point of the CCD^a

Anion	TP (m)	k'
Fluoride	9460	0.80
Chloride	21 000	2.72
Nitrite	18 500	4.51
Bromide	26 300	7.53
Nitrate	24 000	10.41
Sulphate	18 500	4.21
Phosphate	11 400	10.24

^a Eluent composition: 0.6 mM HClO₄, 60 mM NaOH, 10 mM Na₂CO₃ (coded units: 0/0/0).

degree of crosslinking, the reactivity is high enough to give exchange capacities of about 600 $\mu\text{equiv./g}$.

3.2. Performance of the separation column

The chromatographic performance of surface-functionalised, high-capacity anion exchangers is often very poor with theoretical plate numbers less than 10 000 per meter. Besides the lack of conductivity detection, this may be another reason for the minor use of high-capacity anion exchangers in ion chromatography. Table 2 shows the average theoretical plate numbers for the separation column employed at the center point of the central composite design. With exception of fluoride and phosphate, the theoretical plate numbers range from 20 000 to 26 000, which are excellent values for a high-capacity anion exchanger. The plate numbers are two- to three-times higher than those obtained with a chloromethylated packing of the same substrate, functional group and similar exchange capacity [16]. An explanation for this phenomenon is given by several authors [22,23]. The chromatographic efficiency of the high-capacity column used in this study is comparable to commercially available, PS–DVB-based surface functionalised, low-capacity anion exchangers, e.g., Hamilton PRP-X-100 or Star-Ion A 300 [24].

3.3. Retention behaviour of the standard anions

The effect of the concentration of the driving ion on the retention of an analyte ion can be explained by a common retention model for anion chromatography [3]. If some conditions are kept constant, the model can be simplified and the following relationship between the retention factor k' and the concentration of the driving ion c is found:

$$\log k' = -\frac{x}{y} \cdot \log c + \text{const.} \quad (5)$$

In Eq. (5), x is the charge of the analyte ion and y the charge of the driving ion. A plot of $\log k'$ vs. $\log c$ should give a straight line. During an experimental design, all factors (eluent concentrations) are varied at the same time. In this case it is not possible to visualise the retention behaviour of the analytes according to Eq. (5). Nevertheless, an important

conclusion can be drawn. In this study, two monovalent and one divalent driving species are used. According to Eq. (5), the retention of di- or multivalent analytes is stronger influenced by the variation of the eluent concentration than those of monovalent anions, independent of the charge of the driving ion. As a consequence, changes of selectivities should be possible only when analytes differ significantly in their charge.

3.3.1. Chemical properties of the eluents investigated

Table 3 shows some important chemical properties of the eluents investigated. The parameters displayed are calculated with regard to the formation of hydrogencarbonate from carbonate by hydrolysis in water. The dissociation constants used for the calculations were derived from Ref. [25]. They are not corrected for the ionic strength of the eluent or activities of the eluent compounds. Perchloric acid is excluded from the calculations of the pH value since the concentrations of NaOH were corrected for each eluent composition in order to neutralise the amount of perchloric acid used. The effective pH of the eluents undergoes only small changes from 12.27 (eluent 11) to 12.99 (eluent 12). The effective pH therefore seems to be of minor importance for the interpretation of the retention data. In contrast the ionic strength varies from 29.49 (eluent 11) to 69.63 mM (eluent 12).

The effective concentrations of hydroxide differs only slightly from the theoretical concentrations (Table 1) because of the formation of HCO_3^- from the reaction of CO_3^{2-} with water. The highest deviation from the theoretical value (6.2%) is observed at eluent 11. With regard to the effective concentrations of bicarbonate and carbonate as well as to the resulting effective charge, the formation of HCO_3^- is negligible for the discussion of the retention data. The molar ratio of hydrogencarbonate to carbonate is always smaller than 0.005 resulting in an effective charge of carbonate of more than 1.99 for each eluent composition. Therefore the only driving carbonate species is CO_3^{2-} since the species distribution of carbonate is almost independent of the eluent composition or the effective pH.

Phosphate is the only analyte investigated whose charge is dependent on the eluent pH. Therefore

Table 3

Important chemical properties of the eluents investigated in consideration of the carbonate–hydrogencarbonate equilibrium (in addition, the distribution of the phosphate species and the resulting effective charge of phosphate are displayed for each eluent composition)

Eluent	Effective pH ^a	Ionic strength (mM) ^a	c(OH ⁻) (mM) ^a	c(HCO ₃ ⁻) (mM) ^a	c(CO ₃ ²⁻) (mM) ^a	Effective charge carbonate	c(HPO ₄ ²⁻) (%) ^b	c(PO ₄ ³⁻) (%) ^b	Effective charge phosphate
1	12.59	29.73	39.14	0.03	4.97	1.99	28.20	71.18	2.70
2	12.59	29.93	39.14	0.03	4.97	1.99	28.20	71.18	2.70
3	12.90	49.75	79.14	0.01	4.99	2.00	16.68	83.32	2.83
4	12.90	49.95	79.14	0.01	4.99	2.00	16.68	83.32	2.83
5	12.58	49.28	38.40	0.08	14.92	1.99	29.22	70.78	2.71
6	12.58	49.47	38.40	0.08	14.92	1.99	29.22	70.78	2.71
7	12.89	69.34	78.40	0.04	14.96	2.00	16.86	83.18	2.83
8	12.89	69.53	78.40	0.04	14.96	2.00	16.86	83.18	2.83
9	12.77	49.41	58.72	0.02	9.96	2.00	21.25	78.75	2.79
10	12.77	49.80	58.72	0.02	9.96	2.00	21.25	78.75	2.79
11	12.27	29.49	18.72	0.11	9.89	1.99	45.84	54.16	2.54
12	12.99	69.63	98.72	0.02	9.98	2.00	13.83	86.17	2.86
13	12.77	30.30	60.00	0.00	0.00	0.00	20.90	79.10	2.79
14	12.77	29.25	58.13	0.07	19.93	2.00	21.42	78.58	2.79
15	12.77	49.61	58.72	0.04	9.96	2.00	21.25	78.75	2.79

^a Calculated with regard to the formation of HCO₃⁻ from hydrolysis of Na₂CO₃ in water. H₂CO₃ = H⁺ + HCO₃⁻; K₁ = 4.47 · 10⁻⁷ [25], HCO₃⁻ = H⁺ + CO₃²⁻; K₂ = 4.68 · 10⁻¹¹ [25].

^b Calculated for the effective pH of each eluent composition in consideration of the equilibrium. HPO₄²⁻ = H⁺ + PO₄³⁻; K₃ = 4.73 · 10⁻¹³ [25].

Table 3 is completed by percentile amounts of HPO₄²⁻ and PO₄³⁻ in dependence on the eluent composition. The resulting effective charge of phosphate varies from 2.54 at pH 12.27 (eluent 11) to 2.86 at pH 12.99 (eluent 12) which may to a certain extent have an influence on the retention behaviour observed for phosphate.

3.3.2. Variation of perchlorate content

Fig. 3 shows two chromatograms representing the experiment Nos. 9 and 10 of the design matrix, where the concentration of perchlorate in the eluent was altered from 0.2 (-2) to 1.0 mM (+2) while the concentrations of hydroxide and carbonate were kept constant. Therefore the pH as well as the ionic strength of the eluent is constant. At a concentration of 0.2 mM, all analytes are baseline-resolved within 25 min (Fig. 3a). Changing the perchlorate content to 1 mM, the chromatogram is compressed resulting in a coelution of nitrite and sulphate as well as nitrate and phosphate (Fig. 3b). Nitrite, bromide and nitrate seem to be stronger influenced by the variation of the perchlorate content than the other anions. Probably the retention order of nitrite/sulphate and nitrate/

phosphate will reverse at higher perchlorate concentrations. From the retention model for anion chromatography it is expected that the variation of the concentration of a monovalent driving ion on the retention multivalent analytes is significantly higher than on the retention of monovalent analytes like sulphate or phosphate [3]. As demonstrated in Fig. 3, this assumption cannot be confirmed for the variation of perchlorate.

3.3.3. Variation of the hydroxide content

The influence of the variation of the hydroxide content is shown in Fig. 4. The two chromatograms represent the experiments Nos. 11 and 12, where the hydroxide concentration is increased from 20 mM to 100 mM at a constant content of perchlorate (0.6 mM) and carbonate (10 mM). At a concentration of 20 mM NaOH, all analytes are separated within 35 min with a high selectivity for phosphate eluting 15 min after nitrate (Fig. 4a). By increasing the hydroxide content to 100 mM, all peaks were shifted to shorter retention times, but in contrast to the variation of perchlorate, the retention order of the analytes has drastically changed (Fig. 4b). Sulphate

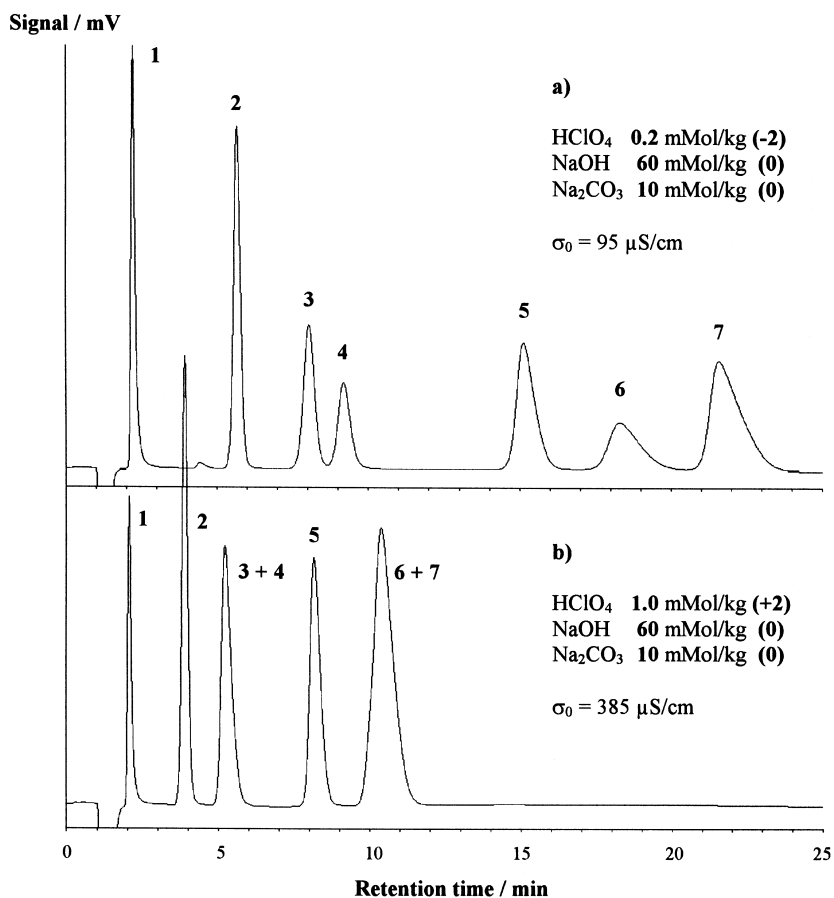


Fig. 3. Selectivity variations of the anions investigated in dependence on the perchlorate content of the eluent. σ_0 = Background conductivity. Analytes: 1 = fluoride; 2 = chloride; 3 = sulphate (10 mg/kg each); 4 = nitrite; 5 = bromide; 6 = nitrate; 7 = phosphate (20 mg/kg each).

is now eluted in front of nitrite while phosphate is shifted from 32 to 7 min. While the retention behaviour of sulphate is consistent with the retention model, the dramatic shortening of the retention times for phosphate is somewhat surprising. Considering the data from Table 3, the effective pH increases from 12.27 (eluent 11) to 12.99 (eluent 12). Therefore the effective charge of phosphate increases from 2.54 to 2.86 due to further dissociation of HPO_4^{2-} to PO_4^{3-} . At first sight longer retention times for phosphate are to be expected since the affinity to the stationary phase increases with the charge of the analyte. But the effect of increasing charge seems to be negligible compared to the increase of elution

power due to the higher hydroxide content. As it is expected from the retention model, the effect of increasing hydroxide concentration on the retention rises with increasing effective charge of the analytes. But the extend of the influence of hydroxide on the retention of phosphate cannot satisfactorily be explained with the variation of the effective eluent pH and the corresponding changes of the effective charge of phosphate (Table 3). Nevertheless, the hydroxide dependent changes of the retention times of phosphate and sulphate, whose effective charge is constant, are to a certain extend corresponding with the common retention model for anion chromatography since the variation of the concentration of a

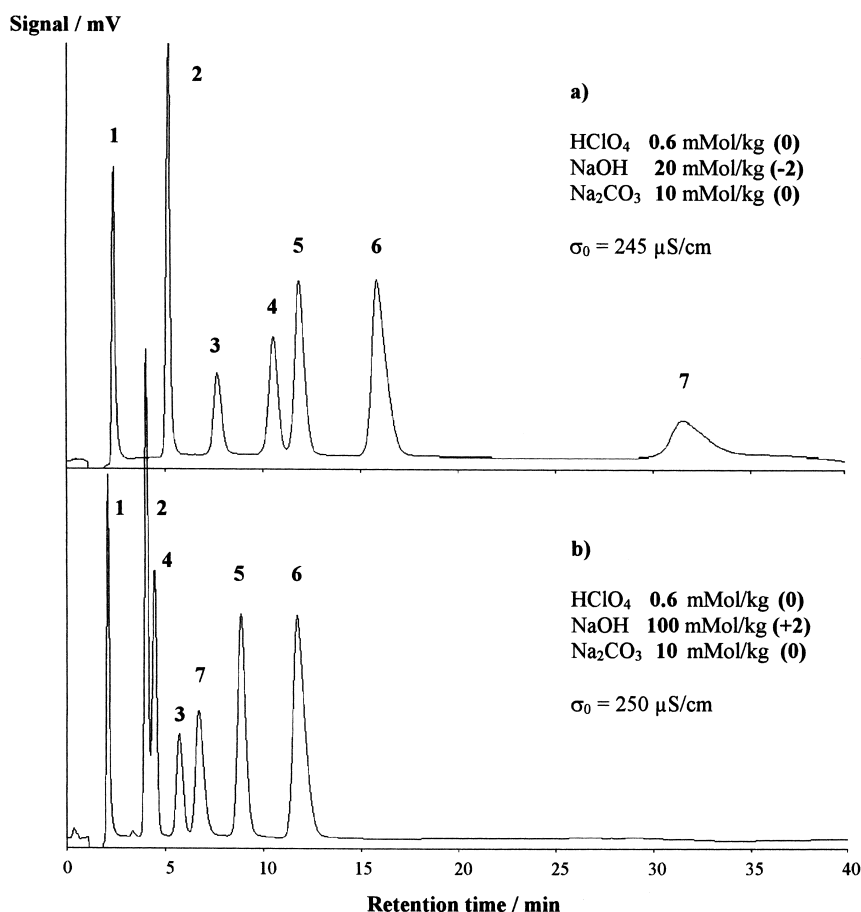


Fig. 4. Selectivity variations of the anions investigated in dependence on the hydroxide content of the eluent. σ_0 = Background conductivity. Analytes: 1 = fluoride; 2 = chloride; 3 = nitrite; 4 = sulphate; 5 = bromide; 6 = nitrate; 7 = phosphate (analyte concentrations as in Fig. 3).

monovalent driving ion has a greater influence on multivalent analytes than on monovalent.

3.3.4. Variation of the carbonate content

The effect of the variation of the carbonate content on the retention of the anions investigated at constant concentrations of perchlorate and hydroxide is similar to the variation of hydroxide, as shown in Fig. 5, where the carbonate content was changed at constant concentrations of perchlorate and hydroxide (experiment Nos. 13 and 14). The influence of the carbonate content on the retention of the multivalent anions sulphate and phosphate is significantly higher than the effect on monovalent analytes. In Fig. 5a (0 mM carbonate), a high selectivity for phosphate is observed. By altering the carbonate content to 20 mM

(Fig. 5b), sulphate is eluted in front of nitrite while phosphate is shifted from 37 to 8 min, now eluting in front of bromide. The observations are consistent with the conclusions drawn from the retention model. The strong effect of carbonate on the retention of sulphate and especially phosphate cannot be explained by variations of the eluent pH. The effective pH and so the species distribution of phosphate are nearly independent from the composition of eluents 13 and 14 (Table 3).

3.4. Statistical analysis of the retention data

3.4.1. Model equations

The retention data for each anion investigated was mathematically fitted by means of a response surface

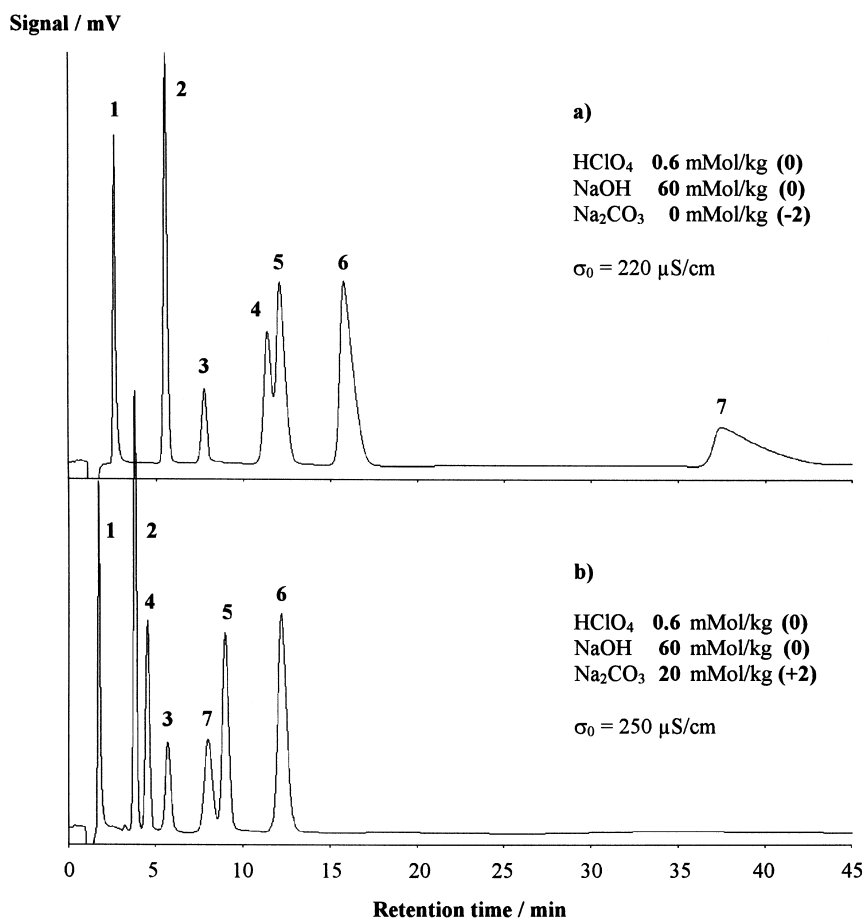


Fig. 5. Selectivity variations of the anions investigated in dependence on the carbonate content of the eluent. σ_0 = Background conductivity. Analytes: 1 = fluoride; 2 = chloride; 3 = nitrite; 4 = sulphate; 5 = bromide; 6 = nitrate; 7 = phosphate (analyte concentrations as in Fig. 3).

regression (RSR) postulating a quadratic model including interaction terms according to Eq. (3). Table 4 shows the estimated coefficients for the

retention factor of each anion resulting from the analysis of the retention data performed on the coded variables.

Table 4

Estimated regression coefficients for retention factors k' using a full quadratic model including second-order and interaction terms [the regression equations are presented in coded forms. (A: $c(\text{HClO}_4)$; B: $c(\text{NaOH})$; C: $c(\text{Na}_2\text{CO}_3)$). Coefficients marked with asterisks are not of statistical significance ($P < 95\%$). R^2 is the quadratic correlation coefficient, D is the deviation of regression]

Anion	y	x_A	x_B	x_C	x_{AA}	x_{BB}	x_{CC}	x_{AB}	x_{AC}	x_{BC}	R^2	D
Fluoride	0.794	-0.048	-0.087	-0.113	-0.011	-0.003*	0.026	-0.002*	0.015	0.032	0.977	0.024
Chloride	2.704	-0.367	-0.290	-0.290	0.059	0.009	0.072	0.005	0.060	0.100	0.991	0.053
Nitrite	4.486	-0.738	-0.457	-0.412	0.136	0.010*	0.085	0.042*	0.103	0.119	0.988	0.106
Bromide	7.493	-1.391	-0.683	-0.613	0.295	-0.001*	0.122	0.056*	0.188	0.195	0.986	0.205
Nitrate	10.364	-2.216	-1.004	-0.790	0.555*	0.031*	0.155	0.100*	0.258	0.320	0.989	0.273
Sulphate	4.149	-0.659	-1.393	-1.382	0.080	0.246	0.423	0.181	0.220	0.589	0.997	0.117
Phosphate	10.239	-2.088	-6.035	-6.284	0.270	1.307	2.266	1.032	1.123	3.454	0.993	0.803

The parameter y represents the intercept of the equation, corresponding to the estimated retention factors at the center point of the experimental domain where all factors assume the coded level 0 (0.6 mM ClO_4^- , 60 mM OH^- , 10 mM CO_3^{2-}). x_A , x_B and x_C are the first-order parameters for each factor (eluent concentration). They represent the main-effects and describe the variation of the retention factor k' corresponding to the increase of one coded unit of each factor (0.2 mM ClO_4^- , 20 mM OH^- , 5 mM CO_3^{2-}). If, for example, the concentration of carbonate in the eluent is increased from level 0 (10 mM) to level 1 (15 mM), a decrease of the predicted retention factor for phosphate of -6.035 units is observed. As expected, all main-effects have a negative sign since the retention factor has to decrease with increasing eluent concentration. All first-order parameters are of statistical significance ($P \geq 95\%$). The ratio of the absolute values of the coefficients x_A , x_B and x_C undergoes significant changes from anion to anion. While for nitrate, coefficient x_A (perchlorate) is twice as high as x_B (hydroxide) and x_C (carbonate), the ratio is reversed for phosphate, for which x_B and x_C are three-times higher than x_A . This means an indication for a higher influence of perchlorate on the retention of nitrate compared to hydroxide and carbonate. For phosphate, the opposite seems to be true.

The quadratic parameters x_{AA} , x_{BB} and x_{CC} describe curvature effects which are to be expected because of the (theoretically) exponential dependence of the retention factor on the eluent concentration [3]. With one exception, all x_{AA} and x_{CC} coefficients are of statistical significance. Most of the x_{BB} quadratic terms fail to be significant. Note that the

sign of the quadratic terms is positive in most cases. For monovalent anions, the absolute values of the quadratic terms are one-order of magnitude lower than those of the main factors. Only for phosphate, they play a major role.

The interaction parameters x_{AB} , x_{AC} and x_{BC} responsible for curvature and twisting effects of the response surfaces. They are with one exception positive in sign. While interactions between perchlorate and hydroxide are not significant in most cases, perchlorate–carbonate and hydroxide–carbonate interactions are always significant. With exception of sulphate and phosphate, the interaction terms are of minor importance for the retention of the anions investigated.

The importance of the different kind of terms becomes more clear from Table 5, in which the contribution of linear, quadratic and interaction terms to the complete regression equation for each anion is presented. The sum of the contributions equals to the quadratic correlation coefficient R^2 . The difference to 100%, which would mean the complete fitting of the measured retention data, is the residual error, representing the sum of the so-called lack of fit and pure error. For monovalent anions, the contribution of linear terms is greater than 89% in all cases. Quadratic and interaction terms are of minor importance. The fitting of experimental data is very good for monovalent anions since the correlation is 97.7% (fluoride) or higher. For sulphate, the contribution of linear terms is somewhat lower compared to monovalent anions, caused by a higher influence of interaction terms. For phosphate, this trend is more pronounced, since linear terms are decreased to 82% for the benefit of quadratic (9.64%) and interaction

Table 5

Contribution of linear, quadratic and interaction terms to the regression polynomials for k' as a result of an analysis of variance (ANOVA) followed by an ϵ^2 -test (all data are in percent)

Anion	Linear	Quadratic	Interaction	R^2	Residual error ^a
Fluoride	89.19	6.11	2.44	97.74	2.26
Chloride	93.58	3.60	2.12	99.11	0.89
Nitrite	93.83	3.63	1.35	98.81	1.19
Bromide	92.25	5.03	1.27	98.55	1.45
Nitrate	90.73	6.96	1.24	98.92	1.08
Sulphate	88.60	6.68	4.42	99.70	0.30
Phosphate	82.35	9.64	7.31	99.31	0.69

^a Residual error = lack of fit + pure error.

terms (7.31%). The correlation for multivalent anions is slightly better compared to monovalent anions ($R^2 > 99\%$).

Table 5 implies that for practical use the retention factors of the anions investigated can be described postulating a full quadratic model including interaction terms although in theory there is an exponential dependence of k' on eluent concentrations. Considering this fact it is somewhat surprising that at least for monovalent anions the retention factors may as well be fitted using only linear terms.

3.4.2. Verification of the model equations

The model equations as presented in Table 4 allow to calculate retention factors at any eluent composition within the experimental design. The very good correlation of the experimental data, expressed by the quadratic correlation coefficient, implies a precise prediction of retention factors. Table 6 shows the results of a comparison of experimental and calculated retention factors. The calculation was done by inserting the corresponding coded concentration units into the model equations. All coefficients were used independent of their statistical significance. The results show that with few exceptions no significant differences between calculated and experimental data are found. It is important to note that the model equation are reasonable only within the experimental domain. They may be applied to outliers, but in this investigation the equations failed to estimate the retention factors correctly even if only one concentration was outside of the concentration ranges investigated.

3.4.3. Examples of response surfaces

The model equations according to Table 4 describe four-dimensional hyper-planes representing the dependence of the retention factor on the varying concentrations of the eluent compounds. If one concentration is kept constant at a medium level (0 in coded units), the dependence may be visualised in a three-dimensional plot. Therefore three response surfaces are necessary if three variables are involved. Note that the surfaces do not display the original data.

Fig. 6 shows the response surfaces for sulphate, based on fitted retention factors. The dimensions of the factors are real concentrations. For coded units, the surfaces would have the same appearance. All planes are similarly shaped since the retention factor of sulphate must decrease with increasing eluent concentrations. The response surfaces show no twisting, an indication for a negligible role of interaction terms. The variation of hydroxide and carbonate concentrations has a much higher influence on the retention of sulphate than the variation of perchlorate which is obvious from the curvature effects (Fig. 6a and b). These conclusions are consistent with the chromatograms (Figs. 3–5). The effects of hydroxide and carbonate are almost equal since the response surface is nearly symmetric in shape.

The response surfaces for nitrate are presented in Fig. 7. In this case, the retention factor is highly influenced by the variation of perchlorate (Fig. 7a and b). The response surfaces seem to be mirror images of those corresponding to sulphate (Fig. 6a and b). As shown in Fig. 7c, the effect of hydroxide

Table 6

Calculated and experimental retention factors k' for two eluent compositions within the experimental design (values in parentheses are coded concentrations)^a

Anion	Calculated 1	Experimental 1	Calculated 2	Experimental 2
Fluoride	0.66±0.02	0.66±0.01	0.86±0.02	0.84±0.01
Chloride	2.48±0.05	2.43±0.02	2.77±0.05	2.65±0.01
Nitrite	4.17±0.11	4.11±0.04	4.44±0.11	4.39±0.03
Bromide	7.16±0.21	7.07±0.05	7.25±0.21	7.24±0.06
Nitrate	10.17±0.27	9.95±0.07	9.90±0.27	9.82±0.02
Sulphate	2.90±0.12	2.85±0.03	5.25±0.12	5.03±0.04
Phosphate	5.89±0.80	5.45±0.05	15.93±0.80	15.75±0.06

^a Eluent 1: 0.5 mM HClO₄; 75 mM NaOH; 17.5 mM Na₂CO₃ (−0.5/0.75/1.5). Eluent 2: 0.75 mM HClO₄; 50 mM NaOH; 7.5 mM Na₂CO₃ (0.75/−0.5/−0.5). For calculations, coded concentrations were inserted in the equations from Table 2. Experimental values are the mean of three runs.

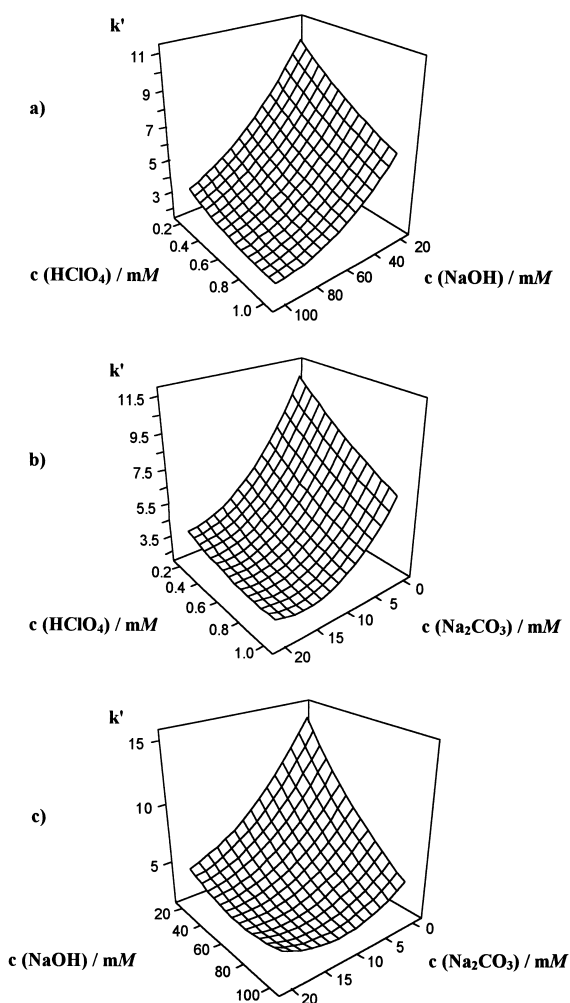


Fig. 6. Response surfaces showing the influence of the eluent compounds on the retention factor k' for sulphate.

is somewhat higher compared to carbonate, but both are of minor importance for the elution of nitrate.

The effects of both monovalent driving ions is remarkable. Perchlorate is a large, polarisable anion of little hydration and has therefore a high affinity to quaternary ammonia groups, resulting in a very high elution power. Hydroxide is small, highly hydrated and of significantly lower elution power than perchlorate. On the other hand, the concentration range investigated for hydroxide are two-orders of magnitude higher, but they were chosen with respect to what is reasonable for the application in anion chromatography. The results lead to the assumption,

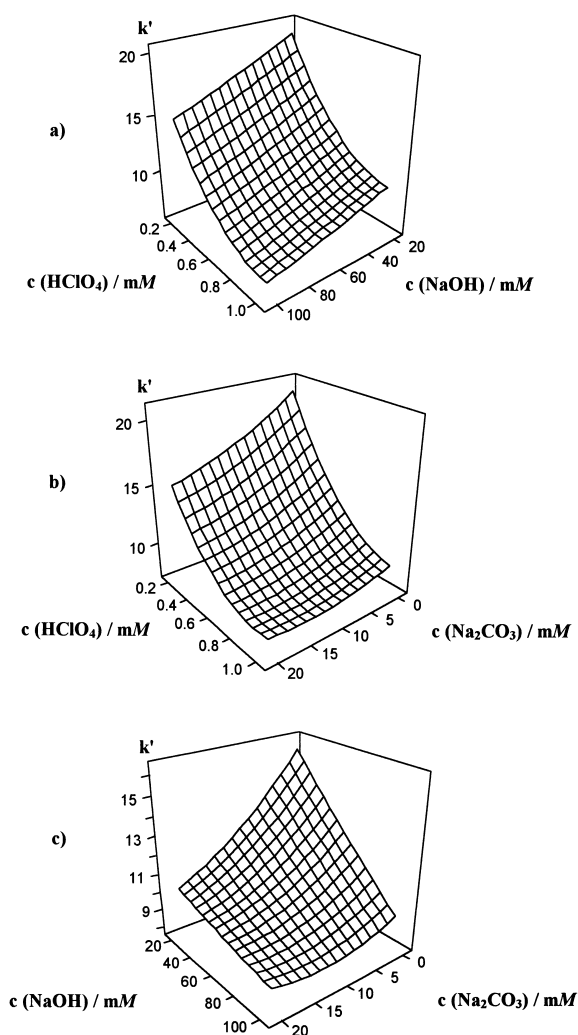


Fig. 7. Response surfaces showing the influence of the eluent compounds on the retention factor k' for nitrate.

that perchlorate is a better eluent for anions that have comparable chemical characteristics like nitrate. The opposite is observed for hydroxide, and, regarding the response surfaces in Figs. 6 and 7, for carbonate.

3.4.4. Effect of the main factors on the retention factors

The effect of the main factors, e.g., variation of eluent concentrations, on the retention factors becomes clearer by further statistical treatment of the data. This was done by a one-way ANOVA. The one-way ANOVA represents the contribution of

variance of a main factor to the total variance. The contribution includes linear and quadratic effects. The variance of a main factor was then related to the total variance (ϵ^2 -test) representing the contribution of the main factor in percent.

The results of these calculations are displayed in Table 7, showing the extend of variation of the retention factor caused by the variation of eluent concentrations within the experimental domain. For monovalent analytes, 97 to 99% of the variation of the retention factor can be explained with main effects. Only for multivalent analytes sulphate and phosphate interaction terms are of importance since the sum of the main effects is smaller than 95%. This is consistent with the conclusions drawn from Table 5. From Table 7 it is obvious that within the concentration ranges investigated the eluent compounds have very different effects on the analytes which can be divided into three groups. The first group are analytes mainly influenced or eluted by hydroxide or carbonate. These analytes are fluoride, sulphate and phosphate. Although perchlorate does of course have an effect on the elution of these anions, the effect is not of statistical significance ($P < 95\%$). As shown in Table 3, the effects of hydroxide and carbonate on the retention of phosphate cannot be satisfactorily explained by the influence of the eluent pH or the carbonate species distribution. The second group, chloride and nitrite, are anions affected by all eluent compounds but with different contributions and the third group, bromide and nitrate, is influenced significantly only by perchlorate with minor effects of hydroxide and carbonate.

The results of Table 7 are somewhat surprising and difficult to explain although the results are in good agreement with the chromatograms obtained

(Figs. 3–5). The main problem is the difference in the concentration range investigated. The perchlorate concentration is two-orders of magnitude lower than the hydroxide range with carbonate lying in-between. On the other hand, the concentration ranges represent the elution power of the eluent anions applied ($\text{ClO}_4^- \gg \text{CO}_3^{2-} > \text{OH}^-$), and the choice of the eluent concentrations is reasonable for practical use.

The first attempt to explain the data from Table 7 was to correlate the effects with the hydrated ionic radii of analyte and eluent anions. The hydrated ionic radii can be calculated from the limiting conductances [26,27]. But the argumentation with hydrated ionic radii is misleading. For example, the hydrated ionic radii of chloride and bromide are 121 and 118 pm, respectively. This would lead to the assumption, that both analytes should be influenced in the same way by the eluent compounds. Furthermore, they should have almost the same retention factors at a given eluent composition. But this assumption is in contrast to the chromatograms (Figs. 3–5) and to the results from Table 7. The reason is that the hydrated ionic radii derived from the limiting conductances do not display chemical properties since two ions, independent of their chemical origin, have the same hydrated ionic radii in case their limiting conductances are equal.

A better approach is to explain the effects from Table 7 considering the unhydrated ionic radii related to the nominal charge. Although this is only a simplification since the effective charges of all anions are significantly smaller than the nominal charge when concentrated eluents and high-capacity anion exchangers are applied [7,28], this model is able to qualitatively explain the effects observed. Table 8 shows the ionic radii of the eluent and

Table 7

Effect of the main factors (eluent compounds) on the retention factors as a result of a one-way ANOVA followed by an ϵ^2 -test [all data are in percent, effects marked with asterisks are not of statistical significance ($P < 95\%$)]

Anion	HClO ₄	NaOH	Na ₂ CO ₃	Sum	Residual error
Fluoride	11.04*	30.60	57.47	99.11	-0.89
Sulphate	9.27*	41.12	44.33	94.72	-5.28
Phosphate	5.39*	39.26	47.69	92.34	-7.66
Chloride	42.81	26.02	28.18	97.02	-2.98
Nitrite	58.28	21.38	18.11	97.78	-2.22
Bromide	69.30	15.79*	12.97*	98.07	-1.93
Nitrate	75.36	14.21*	8.75*	98.33	-1.67

Table 8
Ratios of ionic radii related to nominal charge for eluent and analyte anions

Anion	R (pm) ^a	z ^b	R/z (pm)
Perchlorate	240	1	240
Hydroxide	130	1	130
Carbonate	178	2	89
Fluoride	126	1	126
Sulphate	258	2	129
Phosphate	280 ^c	2.79 ^d	101
Bromide	188	1	188
Nitrate	179	1	179
Chloride	172	1	172
Nitrite	192 ^e	1	192

^a Thermochemical radii [28].

^b Nominal charge.

^c Estimated value, no data available.

^d At pH=12.77 (see Table 3).

^e Large value due to deviation from spherical symmetry.

analyte anions related to their nominal charge. For the eluent ions, the R/z ratio decreases drastically from perchlorate (240 pm) to hydroxide (130 pm) and carbonate (89 pm). In the same way, the extend of hydration increases, leading to the conclusion that perchlorate is a soft and polarisable anion while hydroxide and carbonate are much harder and to a lesser extend polarisable. Regarding the analyte anions, fluoride, sulphate and phosphate have similar R/z ratios ranging from 101 to 129 pm. These anions therefore are hard, strongly hydrated and their retention factors are highly influenced by the hard eluent anions carbonate and hydroxide. Although perchlorate is a very strong driving ion, its effect on strongly hydrated anions is of minor importance since perchlorate is weakly hydrated and polarisable. Therefore the influence of the eluent compounds decreases in the order carbonate > hydroxide >> perchlorate.

The opposite trend is observed for the larger and more polarisable anions bromide ($R/z=188$ pm) and nitrate ($R/z=179$ pm) which are less hydrated. Consequently, the retention factor of these anions is influenced in the order perchlorate >> hydroxide > carbonate. Since nitrate elutes after bromide, it seems to be more polarisable than bromide although nitrate has a smaller ionic radius. This assumption is proved by the higher effect of perchlorate and the smaller

effects of hydroxide and carbonate on nitrate than on bromide (Table 7).

Somewhat difficult to explain are the effects for chloride ($R/z=172$ pm) and nitrite ($R/z=192$ pm), which are significantly influenced by all eluent compounds although perchlorate is of major importance. The large ionic radius of nitrite is caused by its deviation from a spherical symmetry [29]. Considering the ionic radius only, nitrite should show the same behaviour as bromide and nitrate which is in contrast to the chromatograms (Figs. 3–5) and to the results of Table 7. Although chloride is 16 pm smaller than bromide, the difference of the ionic radii is no satisfying explanation for the effects observed. On the other hand, the effect of the eluent compounds on the retention factor for the halide ions investigated correlates with their ionic radii or polarisability. The effect of perchlorate increases in the order $F^- < Cl^- < Br^-$ while the influence of hydroxide and carbonate decreases. If iodide would have been included in this study, the effect of perchlorate on iodine would probably be greater as on bromide with decreasing effects of hydroxide and carbonate.

Although the data available in this study covers the retention behaviour of only seven analyte anions, the results lead to the conclusion that there are interactions between analyte anions and eluent anions during the elution process. The affinity to the functional groups seem to be of minor importance. Considering the effects of Table 7, the following can be stated: hard, strongly hydrated anions (fluoride, sulphate, phosphate) are eluted by hard and strongly hydrated eluent anions (hydroxide, carbonate) while soft and less hydrated anions (bromide, nitrate) are eluted by perchlorate. Analytes in-between these critical cases (chloride, nitrite) are influenced by all eluent compounds. It has to be noted that the effects described are due to a single separation column covering a special kind of functional group of medium polarity. Applying functional groups of different polarity or a different polymer backbone, e.g., methacrylate polymers, the numeric values of the effects may found to be different from this study. For example, functional groups of higher polarity (e.g., triethanolamine) will have a higher affinity to hydroxide which is known as hydroxide selectivity [3]. Therefore the effect or elution power of hy-

droxide on such stationary phases will be more pronounced [28].

3.5. Application of the novel elution system to samples of high matrix content

To demonstrate the potential of high-capacity anion chromatography and conductivity detection the novel elution system is applied to samples with high matrix content. Fig. 8 shows a chromatogram of a sample containing 1000 mg/l H_2PO_4^- spiked with fluoride, chloride, sulphate and nitrate (1 mg/l each). Although there is a baseline drift due to matrix effects, all analytes are well resolved from the phosphate peak. Compared to a standard chromatogram with the same eluent composition (Fig. 4a), no shift of retention times or decrease of separation efficiency or selectivity was found.

The determination of trace anions (1 mg/l) in a NH_4F matrix (10 000 mg/l $\text{F}^- \approx 2\%$, w/w, NH_4F) is shown in Fig. 9. Unfortunately the chloride peak is

disturbed due to baseline deviation caused by the fluoride matrix, while sulphate and nitrate are well resolved. Again, the retention times of the analytes are not influenced by the matrix. The separation of chloride from the fluoride peak may be enhanced by further optimisation of the eluent composition. Considering the conclusions from Table 7, this could be done increasing the carbonate and decreasing the perchlorate content of the eluent.

4. Conclusions

The novel ternary elution system based on perchlorate, hydroxide and carbonate offers the possibility to apply conductivity detection as the most universal detection technique in ion chromatography to anion-exchange columns of more than 400 μequiv . The sensitivity of detection is limited due to the non-suppressible perchlorate. The background

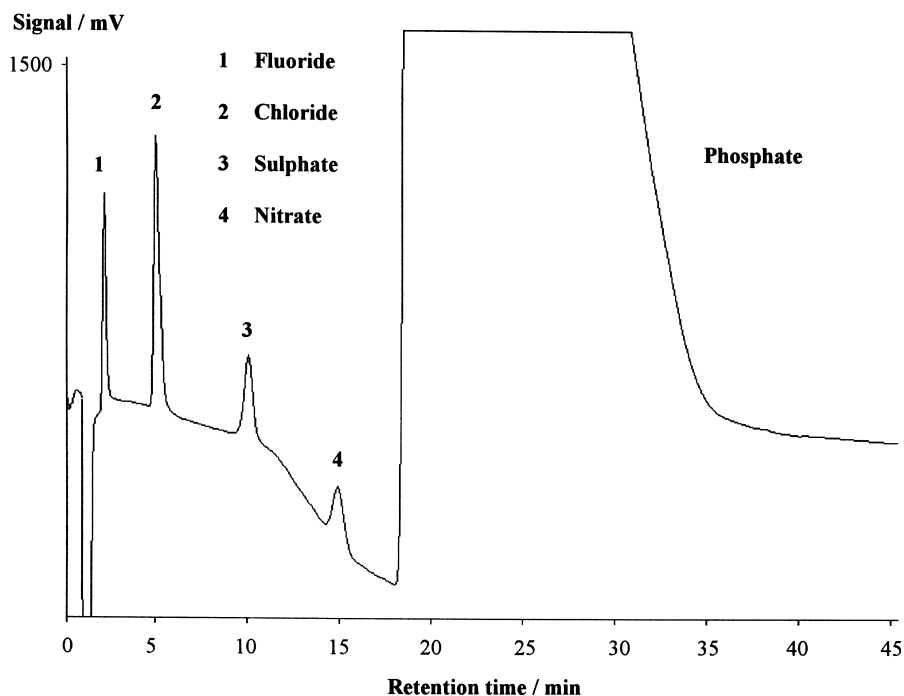


Fig. 8. Determination of trace anions (1 mg/l each) in 1000 mg/l H_2PO_4^- matrix. Chromatographic conditions: 0.6 mM HClO_4 , 20 mM NaOH , 10 mM Na_2CO_3 ; flow-rate: 1 ml/min; injection volume 100 μl ; suppressed conductivity detection.

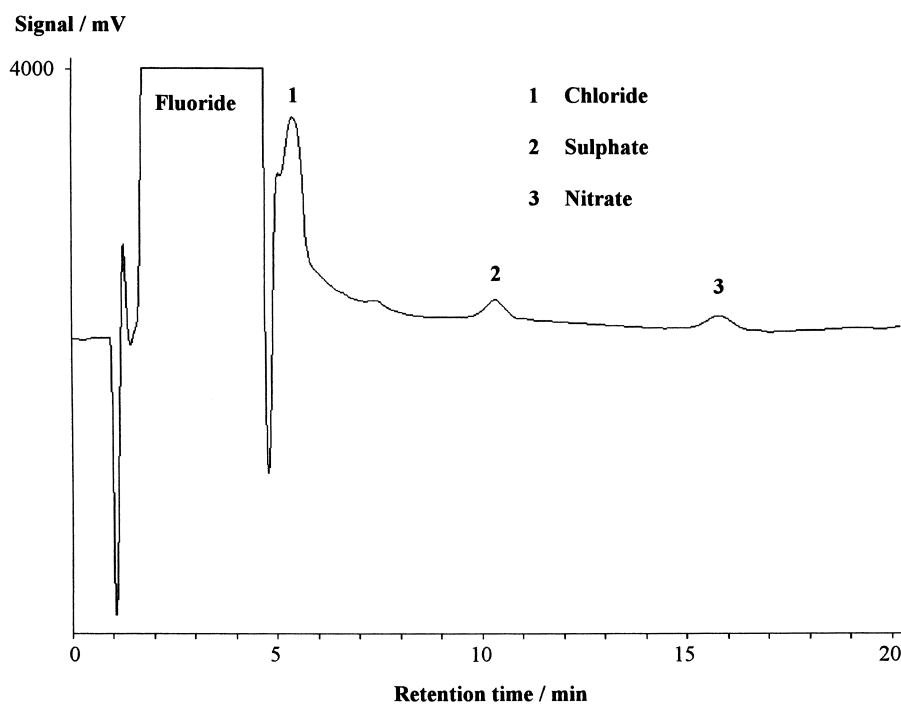


Fig. 9. Determination of trace anions (1 mg/l each) in 10 000 mg/l F^- matrix ($\approx 2\%$, w/w, NH_4F). For chromatographic conditions see Fig. 8.

conductivity varies from 90 to 380 $\mu S/cm$, and for a typical eluent composition, the background conductance of the eluent is comparable to those observed in non-suppressed conductivity detection (180 $\mu S/cm$). The characterisation of the novel elution system by means of a statistical approach shows that the three eluent compounds have very different effects on the retention of the anions investigated. Whereas hard and strongly hydrated anions like fluoride or sulphate are mainly eluted by hydroxide and carbonate, the opposite is found for large and weakly hydrated analytes like bromide and nitrate which are significantly influenced by perchlorate only. To a certain extent, the retention behaviour observed can be explained with the relation of ionic radii and charge of both analyte and eluent anions. The use of model equation enables to predict retention times of the analytes in dependence on the eluent composition which is very helpful for solving analytical problems. The application of the novel elution system to samples of high ionic content shows the potential of

high-capacity anion chromatography with conductivity detection.

Future work will include the application of high-capacity anion chromatography with conductivity detection to real world samples as well as the investigation of the retention behaviour of anions covering a wider range of chemical properties. Furthermore, the effect of eluent compounds on the analytes has to be investigated in dependence of the polarity of the functional group or polymer backbone.

Acknowledgements

Financial support from the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF) and the Fonds der Chemischen Industrie (FCI) is gratefully acknowledged. The authors would also like to thank Dr. Helwig Schäfer (Metrohm,

Switzerland) for providing parts of the chromatographic equipment.

References

- [1] J. Weiss, Ionenchromatographie, 2nd ed., Verlag Chemie, Weinheim, 1991.
- [2] D.T. Gjerde, J.S. Fritz, Ion Chromatography, 2nd ed., Hüthig, Heidelberg, 1987.
- [3] P.R. Haddad, P.E. Jackson, in: Ion Chromatography – Principles and Applications, Journal of Chromatography Library, Vol. 46, Elsevier, Amsterdam, 1990.
- [4] K. Köhler, M. Nowak, A. Seubert, Fresenius J. Anal. Chem. 358 (1997) 551.
- [5] M. Nowak, A. Seubert, Anal. Chim. Acta 359 (1998) 193.
- [6] M. Nowak, G. Schminke, K. Köhler, H. Schäfer, A. Seubert, poster presented at the 10th International Ion Chromatography Symposium, Santa Clara, CA, 1997.
- [7] G. Petzold, Ph.D. Thesis, University of Hannover, Hannover, 1995.
- [8] L. Eek, N. Ferrer, J. Chromatogr. 332 (1985) 491.
- [9] Product Selection Guide, Dionex Corporation, Idstein, 1998.
- [10] J. Diemer, K.G. Heumann, Fresenius J. Anal. Chem. 357 (1) (1997) 74.
- [11] K. Ito, Anal. Chem. 69 (1997) 3628.
- [12] F. Vlácil, I. Vinš, J. Chromatogr. 391 (1987) 133.
- [13] M. Otto, Chemometrics, Verlag Chemie, Weinheim, 1997.
- [14] K. Doerffel, Statistik in der Analytischen Chemie, 5th ed., VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1990.
- [15] S.J. Haswell (Ed.), Practical Guide to Chemometrics, Marcel Dekker, New York, 1992.
- [16] K. Köhler, Ph.D. Thesis, University of Hannover, Hannover, 1998.
- [17] M. Tomoi, N. Kori, H. Kakiuchi, React. Polym. 3 (1985) 341.
- [18] G. Contarini, R. Leardi, J. High Resolut. Chromatogr. 17 (1994) 91.
- [19] Minitab User's Guide, Release 12, Minitab Inc., State College, PA, USA, 1998.
- [20] L.M. Warth, Ph.D. Thesis, Iowa State University, 1988.
- [21] L.M. Warth, J.S. Fritz, J. Chromatogr. Sci. 26 (1988) 630.
- [22] R.M. Diamond, J. Phys. Chem. 67 (1963) 2513.
- [23] R.E. Barron, J.S. Fritz, J. Chromatogr. 284 (1984) 13.
- [24] Metrohm IC Application Notes, Metrohm LTD, Herisau, 1998.
- [25] A.F. Holleman, E. Wiberg, Lehrbuch der Anorganischen Chemie, 91–100th ed., Walter de Gruyter, Berlin, 1985.
- [26] Handbook of Chemistry and Physics, 73 ed., CRC Press, Boca Raton, FL, 1992–1993.
- [27] G. Wedler, Lehrbuch der Physikalischen Chemie, 3rd ed., Verlag Chemie, Weinheim, 1988.
- [28] M. Nowak, Ph.D. Thesis, University of Hannover, Hannover, 1999.
- [29] H.D.B. Jenkins, K.P. Thakur, J. Chem. Educ. 56 (1979) 576.