Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1026 (2004) 195–200
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Coupled ion chromatography for the determination of chloride, phosphate and sulphate in concentrated nitric acid

Magdalena Biesaga [a], Nicole Schmidt [b], Andreas Seubert [b,*]

[a] *Laboratory for Flow Analysis and Chromatography, Department of Chemistry, Warsaw University, Pasteura 1, Warsaw 02-093, Poland*
[b] *Analytical Chemistry, Department of Chemistry, Philipps-University Marburg, Hans-Meerwein-Str., Marburg 35043, Germany*

Received 21 February 2003; received in revised form 31 October 2003; accepted 3 November 2003

Abstract

A coupled ion chromatography (IC) system was used for the determination of chloride, sulphate and phosphate in high-purity nitric acid. Such a high ionic strength matrix causes a selectivity problem in single IC systems. The first part of the system is used for a pre-separation of the analytes from the nitrate matrix. A specially designed high-capacity anion exchanger with low retention for the analytes and high retention for nitrate was developed. The eluent stream containing the analytes was transferred to the second part of the system via a heart-cut valve and a pre-concentration column. The second system utilizes a high performance anion exchanger and is used to quantify the analytes. Recoveries of the analytes are 80–100% for phosphate, and around 100% for sulphate and chloride. Detection limits for chloride, sulphate and phosphate in concentrated nitric acid (69% w/w) are 0.1, 1 and 5 mg/l, respectively.

Keywords: Chloride; Phosphate; Sulphate; Nitric acid

1. Introduction

There is an important analytical task to determine trace amounts of ions in a highly concentrated matrix. This may be the case in speciation analysis, quality control of high-purity chemicals or the monitoring of water disinfection by-products, where the analyte ion concentrations are several orders of magnitude lower than matrix ion concentrations. If the matrix ions cannot be eliminated or reduced, they will in most cases strongly interfere with the separation process which will result in a significant loss of separation efficiency due to column overload or peak overload. The application of ion chromatography (IC) for the analysis of anions in highly concentrated chemicals suffers from a sensitivity problem. Samples need to be diluted with a large volume of water to reduce matrix effects [1]. In order to improve detection limits, column switching techniques using on-line sample pre-treatment to eliminate matrix interferences have been recently developed [2–7], where ion exclusion column was used prior to IC analysis.

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 IC. Low-capacity anion exchangers encounter problems, when trace anions have to be monitored in samples with high matrix contents. High-capacity anion exchangers enable the analysis of samples of high ionic strength without matrix elimination [8,9]. In addition, the use of large injection volumes or more concentrated samples is possible. Kaiser et al. [10] described the application of high-capacity anion exchange columns for the determination of trace anions in a matrix containing a high concentration of nitrate ions. Limits of detection for chloride, phosphate and sulphate were around 150 μg/l for the solution, not for the acid representing the matrix. These limits are still too high for the determination of trace anions in highly concentrated nitric acid, where concentrations of contaminants are at the low μg/l level after the required dilution of 1:100 to 1:1000.

This work discusses the performance of a coupled IC system for trace anion determination in concentrated nitric acid. The system utilizes a specially designed, home-prepared high-capacity anion exchanger for sample pre-separation.

* Corresponding author. Tel.: +49-6421-28-25661; fax: +49-6421-28-22124.
E-mail address: seubert@staff.uni-marburg.de (A. Seubert).

0021-9673/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2003.11.001

Table 1
Optimized operating conditions of the presented coupled IC system for trace determination of chloride, phosphate and sulphate

IC System 1	
Separation column	DVB-Polymer, 4.5 μm particle size, DEMA functional group, 405 μmol/column (Cl^-), 120 mm × 4 mm i.d. PEEK
Eluent	0.1 M NaOH at 1 ml/min
Suppression	Packed bed suppressor, regenerated with 0.1 M HNO_3 at 0.3 ml/min
Loop size	200 μl
Valve 2	
Heart-cut time	2.9–5.2 min (standards), 2.9–4.4 min (samples)
IC System 2	
Pre-concentration column	Dionex Ion-Pac TAC-2 (see Table 2)
Analytical column	Metrohm ASupp 5, 40 μmol/column (Cl^-), 100 mm × 4 mm i.d. PEEK
Eluent	2.5 mM Na_2CO_3, 0.5 mM $NaHCO_3$ at 0.7 ml/min
Suppression	Dionex membrane suppressor, regenerated with 0.025 M H_2SO_4 at 1 ml/min

2. Experimental

2.1. Chromatographic equipment

Two on-line coupled IC systems from Metrohm (Herisau, Switzerland) were used. Each unit consisted of an IC Pump 709 with pulse dampener, a six-port valve, a conductivity detector 732 IC with a suppressor module 753 IC or 793. Both systems and an additional automated six-port stainless-steel valve from Valco were controlled by Metrohm software IC-Net 2.1 via PC computer and 762 IC interface. All columns, tubing, fittings and pump for System 2 were made of polyether–ether–ketone (PEEK). All other chromatographic details are given in Table 1.

2.2. High-capacity stationary phase for sample pre-separation

The stationary phase was prepared by using a self-made polystyrene/divinylbenzene copolymer (PS/DVB) with a particle diameter of about 4.5 μm which was functionalized with 5-bromo-1-pentene in a Friedel–Crafts alkylation step and then aminated with *N*-methyldiethanolamine. The capacity of the final anion exchanger was 580 μmol/g.

2.3. Chemicals

Suprapure grade 69% nitric acid was obtained from BASF AG (Ludwigshafen, Germany). Na_2CO_3 and 30% NaOH were suprapure grade, all other chemicals were pro analysis grade and were obtained from Merck. High-purity water (Millipore Elix/Gradient, Millipore, Eschborn, Germany) was used to prepare all standards and eluents. Anion standards (1000 mg/l) for chloride, sulphate, phosphate were prepared from sodium salts. Working standards were prepared weekly by diluting the 1000 mg/l standards to the appropriate 10–5000 μg/l concentration range.

2.4. Concentrator columns

Three concentrator columns as described in Table 2 were tested for their applicability as pre-concentration device for the effluent of the pre-separation system.

2.5. System operation

Fig. 1 presents the scheme of the coupled IC system. System 1 is linked to System 2 via a time-programmed valve 2 and the concentrator column mounted on valve 3. System 1 is a matrix-overloaded pre-separation system with a self-made high-capacity anion exchanger. System 2 is equipped with a Metrohm ASupp5 commercial analytical column for anion separation with highest performance in terms of efficiency. Valve 2 is time-programmed and allows transferring the effluent from Systems 1 to 2. When valve 2 is in the 'waste' position, the effluent from System 1 goes directly to waste. During 'heart-cut', the valve 2 is switched to the 'sampling' position and the effluent is collected on the concentrator column, which is installed within the six-port sample injection valve 3 (Fig. 2a). Next, 'heart-cut' valve 2 is switched to position 'waste' and the effluent from System 1 goes to waste; at the same moment valve 3 is switched to the injection position in System 2 (Fig. 2b) and the collected sample is then eluted from the concentrator column to the analytical column by the eluent delivered by pump 2.

Table 2
Parameters of concentrator columns used for trace anion pre-concentration

Concentrator column	Stationary phase	i.d. (mm)	Length (mm)	Particle size (μm)	Capacity (μmol per column)
Dionex TAC-2	PS/DVB agglomerated with a quaternary amine functionalized latex	3	35	Unknown	3.4
ShodexCC	Polyvinylalcohol gel chemically bonded with quaternary ammonium	4	25	9	15.8
AG50CC	PS/DVB (BioRad AG 50W-X8) coated with a quaternary amine polyelectrolyte	4	25	150–300	2.8

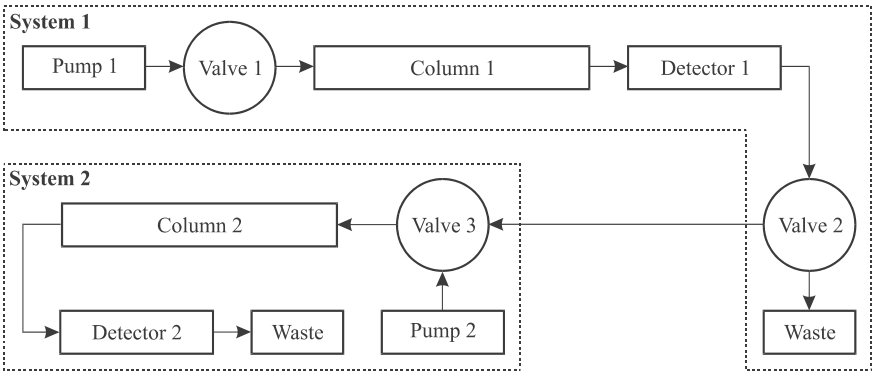

Fig. 1. Scheme of the coupled IC systems.

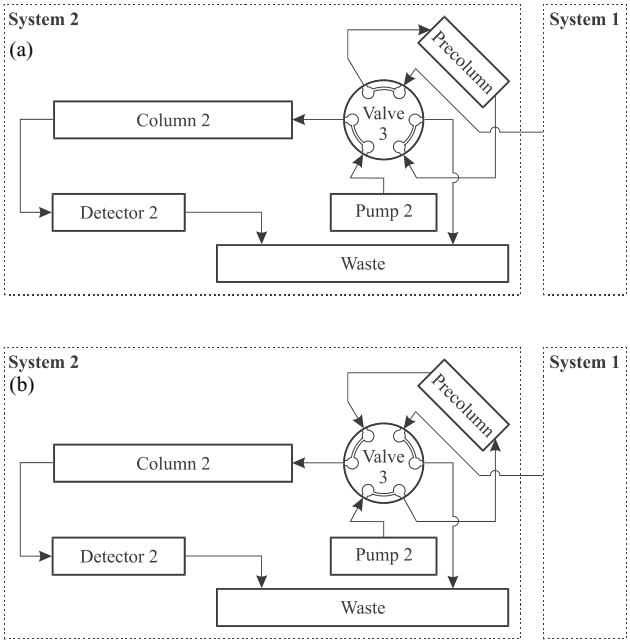

Fig. 2. Valve configuration during (a) sample loading on preconcentrator column in valve 3; (b) injection of sample to System 2.

3. Results and discussion

3.1. High-capacity anion exchange resin

In the pre-separation step, it is important to elute all analytes of interest in front of the matrix anions. The selectivity of ammonia-based anion exchangers always allows sufficient separation of chloride and nitrate. The elution position and order of phosphate and sulphate depends on the specific capacity of the anion exchanger, the polarity of the functional group, the eluent pH, the effective charge of the eluent anion and on the eluent concentration. In general, higher charged analytes are moved to the front of the chromatogram when using a highly concentrated eluent. To maintain retention it is necessary to use columns with a high specific capacity and an eluent with moderate elution strength. When using a hydroxide eluent, phosphate and sulphate are eluted in front of chloride and far in front of nitrate. Sodium or potassium hydroxide can be purchased in sufficient purity, a further prerequisite for ultra-trace analysis. The moderate elution strength of the hydroxide anion is realized by using a polar quaternary ammonium group based on *N*-methyldiethanolamine.

Using triethanolamine for amination should result in better performing columns, but the reactivity of triethanolamine is much lower than that of *N*-methyldiethanolamine, which causes much lower capacity.

3.2. Concentrator column

Several anion exchangers were tested as stationary phases for the concentrator column. The concentrator column was installed in valve 3 and samples were injected directly to System 2 without System 1 being involved. A comparison of peak areas for a 1 ml sample of a 50 μg/l solution of the analyzed trace anions for the concentrator columns described in Table 2 showed that the best results were achieved for the 9 μm ShodexCC material. This column offered the highest peak area for all analytes, while the TAC-2 showed a decreased area for chloride. This trend was even more dominant for the AG50CC column.

The high back pressure of the ShodexCC column makes the operation of the coupled IC system less robust. Therefore, we decided to use the TAC-2 column as the second best choice in terms of performance but the best choice with respect to long-term stability as concentrator column.

3.3. Separation conditions

The application of a high-capacity anion exchanger as stationary phase in System 1 with 0.1 M NaOH as eluent allowed to achieve an order of elution with the nitrate eluting after sulphate, chloride and phosphate. The effluent from System 1 passed through a suppressor column in which a solution of a 0.1 M strong acid was used as regenerant. A notable leakage of the regenerant counter ions from Systems 1 to 2 was always detected in blank sample at a mg/l concentration level. The routinely used sulphuric acid was therefore replaced by nitric acid as regenerant to avoid

sulphate contamination of System 2. Nitrate breakthrough, which indeed occurs at the mg/l level, is no problem because nitrate is the matrix anion.

Optimization of the separation was started by selecting the best conditions for the separation of chloride, phosphate and sulphate from nitrate in System 2. The concentration of carbonate was varied from 2.5 to 10 mM for to achieve a more than 3 min separation between nitrate and the trace anions. The best resolution between nitrate and the analytes was observed at 2.5 mM carbonate for a 250 mm × 4 mm i.d. Metrohm ASupp 5 column. The drawback was a total analysis time of over 50 min. Therefore, we used a shorter column (100 mm × 4 mm i.d.) and an eluent containing 0.5 mM bicarbonate for System 2. The addition of bicarbonate helped to achieve baseline separation between phosphate and sulphate. These changes allowed the reduction of the analysis time in System 2 to less than 17 min.

3.4. Determination of the 'heart-cut' time for sample collection

For the determination of the 'heart-cut' time, a relatively high concentration of chloride, sulphate and phosphate (5 mg/l) was applied. At these concentrations, analyte peaks were easily observed with a high-capacity anion exchanger in System 1. Different ratios in the range from 14:1 to 140,000:1 for nitric acid to analyte concentration were tested. Fig. 3 shows that an increasing concentration of nitric acid slowly moved the phosphate and chloride peaks into the sulphate peak. It should be pointed out that nitrate concentrations exceeding 7000 mg/l (200 μl loop) caused a partial overlap of the phosphate and nitrate peaks. For such high nitrate concentrations, it was necessary to shorten the 'heart-cut' to 2.8–4.4 min after injection of the sample

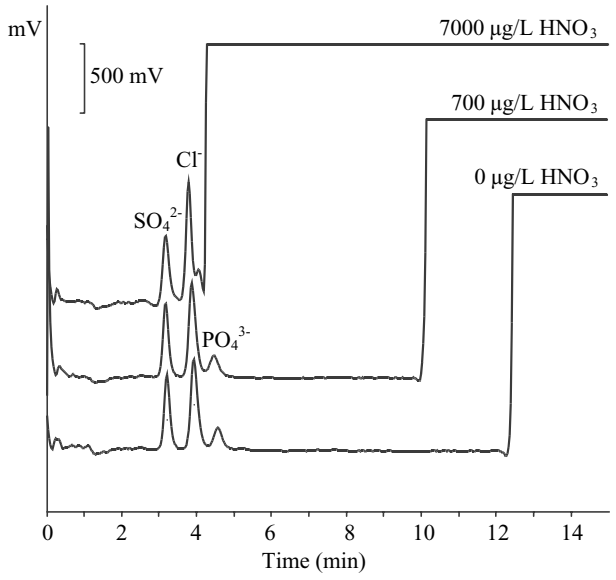

Fig. 3. Influence of nitric acid concentration on heart-cut conditions in System 1; loop, 100 μl; other conditions as in Table 1.

Table 3
Calibration parameters (seven data points) $y = A\,x$ for the three analytes in standard solutions using the heart-cut time 2.8–5.2 min

	System 1 LOD (μg/l)	System 2		
		LOD (μg/l)	A	Correlation
Cl^-	100	0.5	1406.95	0.9999
PO_4^{3-}	500	5	7656.3	0.9994
SO_4^{2-}	250	2.5	1785.07	1

Parameter y is the analyte concentration and x is the peak area. The calibration was forced through zero.

into System 1. During the 'heart-cut', the effluent from the high-capacity anion exchange column was collected on the concentrator column. If the heart-cut time was changed to 2.8–5.2 min, as suggested for pure standards and dilute nitric acid, the recovery for all anions was around 100%.

Injection loops of 100, 200 and 585 μl were tested for application in System 1; the loop of 200 μl was chosen because for this injection volume the peaks of the trace anions were still separated from the nitrate peak. The highest concentration of nitric acid in sample was 7000 mg/l for the 200 μl injection volume in System 1. Otherwise the amount of nitrate collected on the concentrator column disturbs the determination of the trace anions in System 2.

3.5. Method performance

The calibration parameters for a 7-point calibration curve and the detection limits for anions using the coupled IC system are shown in Table 3. The LODs ($S/N > 3$) were calculated based on a 200 μl injection while no matrix is present. The calibration was measured for analyte concentrations from 10 to 1000 μg/l without the addition of nitrate.Chloride and sulphate were determined at low μg/l levels in the 100-fold diluted nitric acid with recoveries of 110 and 98%, respectively; for phosphate the recovery was around 100% in technical acid samples (67% (w/w)) and around 80% for both 69% (w/w) nitric acids. Recoveries are calculated using the calibration shown in Table 3, the R.S.D. for aqueous standards are 2.6% for chloride, 5.40% for phosphate and 4.04% for sulphate ($N = 7$). For 100-fold diluted nitric acid samples, the R.S.D. are 3.5, 6.9 and 3.5% for chloride, phosphate and sulphate, respectively ($N = 5$).

The lower recovery for phosphate in higher concentrated acids was caused by the incomplete separation of the nitrate and the small phosphate peak in both systems. The LODs for 69% nitric acid are given in Table 4.

3.6. Sample analysis

The influence of pH of sample on separation condition was also tested. Fig. 4 shows chromatograms obtained from System 1 for the same ratio of nitrate to trace anion, when one solution was prepared from the acid and the second one from the sodium salt. No significant difference in the

Table 4
LODs and concentration values found for suprapure, analytical and technical grade nitric acid after 1:100 dilution and 200 μl injection; values calculated for the concentrated acid

	Technical grade 65% (mg/l)	Analytical grade 69% (mg/l)	High-purity 69% (mg/l)	LOD for 69% nitric acid (mg/l)
Cl^-	6.5	2.2	0.49	0.1
PO_4^{3-}	<5	<5	<5	5
SO_4^{2-}	6.2	0.7	<5	0.5

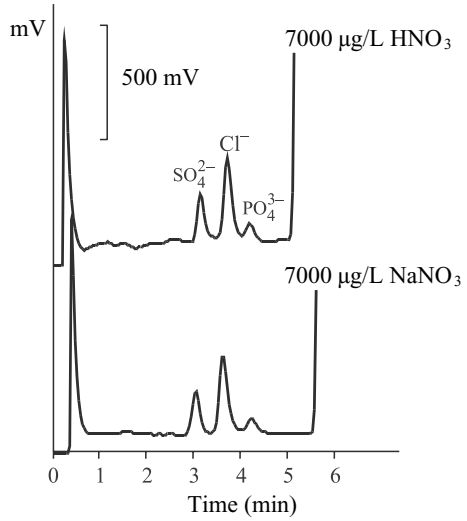

Fig. 4. Chromatograms obtained with System 1 for 5 mg/l chloride, phosphate, sulphate with 7000 mg/l HNO_3 or 7000 mg/l $NaNO_3$. Loop, 100 μl; other conditions as in Table 1.

retention time of the trace anions can be observed and there is obviously no need for neutralization before injection. The method was applied to determine chloride, phosphate and sulphate anions in nitric acid solutions of different quality: technical grade (65% (w/w)), pro analysis (69% (w/w)) and suprapure nitric acid (69% (w/w)). All acids were 100-fold diluted with water before injection. The results are presented in Table 4.

The behavior of System 2 is shown in Fig. 5. The selectivity of the Metrohm ASupp5 is not the best choice for this application, but performance was considered more important than selectivity because of its influence on sensitivity. The nitrate signal (highest peak of Fig. 5 at $t_R = 8.1$ min) is well resolved from all analytes. The system peaks caused by the use of the concentrator column are also well resolved from the analyte signals.

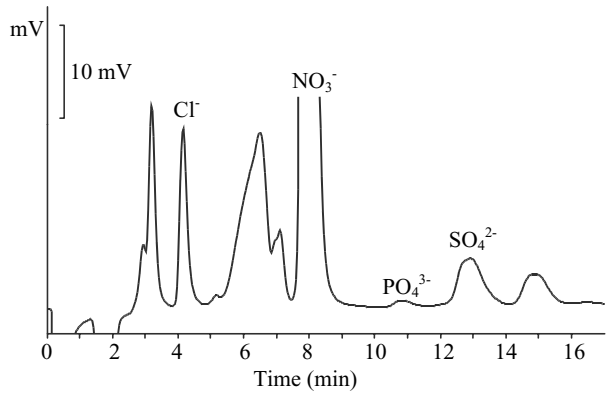

Fig. 5. Chromatogram obtained for System 2 of the coupled IC system for trace anions in technical nitric acid diluted 1:100 with water, and spiked with 100 μg/l of each Cl^-, PO_4^{3-} and SO_4^{2}; other conditions as in Table 1.

3.7. Lifetime of pre-separation column

The lifetime of the pre-separation column is sufficiently high. The capacity decreased from 405 μmol per column (for chloride) to 337 μmol per column over approximately 500 h, which is equivalent to nearly 1000 analysis cycles. Although the separation of the analytes from the nitrate peak decreased slowly, the performance of the method was maintained for capacities above 340 μmol per column.

4. Conclusions

A coupled IC system could be successfully applied for the trace determination of anionic contaminants in concentrated nitric acid without sample preparation if a high-capacity anion exchanger was used in System 1. Chloride, sulphate and phosphate were determined at the low μg/l level when the ratio of the trace anion concentrations to nitric acid was of the order of 1:70,000. The method is fast and sensitive, and can be applied for the routine analysis of trace anion contaminants in highly concentrated nitric acid. The application of a high-capacity anion exchanger in the pre-separation step allowed 200 μl injection volumes for samples containing 7000 mg/l nitric acid without any column damage.

Acknowledgements

The authors would like to thank Metrohm AG, Switzerland, and the Deutsche Metrohm, Filderstadt, for providing the IC equipment. Magdalena Biesaga would like to thank the DAAD for supporting her stay in Germany.

References

[1] E. Smith, Anal. Chem. 55 (1983) 1427.
[2] E. Kaiser, J.S. Rohrer, K. Watanabe, J. Chromatogr. A 850 (1999) 167.
[3] Y. Huang, S.-F. Mou, K.-N. Liu, J.M. Riviello, J. Chromatogr. A 884 (2000) 53.

[4] K. Wang, Y. Lei, M. Eitel, S. Tan, J. Chromatogr. A 956 (2002) 109.
[5] S. Peldszus, P.M. Huck, S.A. Andrews, J. Chromatogr. A 793 (1998) 198.
[6] F.S. Stover, J. Chromatogr. A 956 (2002) 121.
[7] K. Pyrzyńska, E. Poboży, Crit. Rev. Anal. Chem. 32 (2002) 227.
[8] M. Nowak, A. Seubert, J. Chromatogr. A 855 (1999) 91.
[9] K. Kohler, M. Nowak, A. Seubert, Fresenius J. Anal. Chem. 358 (1997) 551.
[10] E. Kaiser, J.S. Rohrer, D. Jensen, J. Chromatogr. A 920 (2001) 127.