

Determination of anions in concentrated nitric acid by ion chromatography: The influence of temperature on column selectivity

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Summary

We have developed a direct injection ion chromatography method for the determination of low levels of anions in a nitrate matrix. Separation on the high-capacity Metrosep A Supp 16 – 250 was achieved by optimizing both eluent composition and column temperature. An eluent composition of 3 mmol/L Na_2CO_3 and 25 mmol/L NaOH and a column temperature of 25 °C yielded an excellent chromatographic separation with nitrate eluting as the last anion.

Calibration curves were linear with a coefficient of determination of 0.9994 or better. Spike recovery percentages for chloride and sulfate in a diluted nitric acid matrix (1:100, w/w) were within 95...102% and 95...106%, respectively. The direct injection arrangement requires no neutralization of the acid and is highly suitable for accurately determining low levels (ppm) of chloride and sulfate in the presence of high quantities of nitrate in the percent range.

Introduction

The determination of anions in concentrated nitric acid is of crucial importance in semiconductor manufacture as even small amounts of ionic impurities significantly affect the efficiency of the production process. Traditional wet chemical methods are labor-intensive, yield poor results and suffer from the health and environmental hazards due to the handling of nitric acid.

Ion chromatography is a very powerful analytical method allowing to reliably determine ionic species. The analytical challenge treated in the present work consists in detecting low concentrations (ppm) of chloride and sulfate in the presence of very high concentrations (percent) of nitric acid or nitrate, respectively.

Due to the high concentrations of nitric acid, the sample can either be neutralized prior to chromatographic separation or be directly injected after a 1:100 (w/w) dilution.

The main objective of this work was to develop a direct injection ion chromatographic method that allows to determine very small chloride and sulfate concentrations in high-nitrate matrices. Therefore the influence of varying eluent composition and column temperature was evaluated. Moreover, calibration linearity and recovery rates for spiked nitric acid samples were determined.

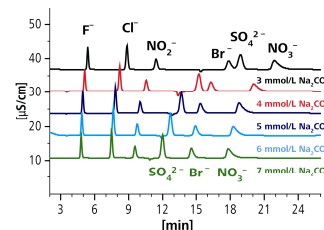
System setup

- 850 Professional IC Anion – MCS
- 858 Professional Sample Processor – Pump
- Metrosep A Supp 16 – 250



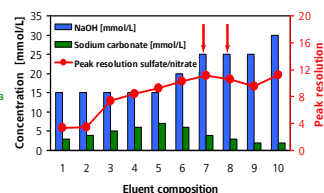
Eluent composition

Column: Metrosep A Supp 16 – 250
Column temp.: 25 °C
Eluent: 3, 4, 5, 6 and 7 mmol/L Na_2CO_3
15 mmol/L NaOH
Flow: 0.8 mL/min
Loop: 20 µL



Increasing the Na_2CO_3 concentration shortens the elution time of all anions.

Column: Metrosep A Supp 16 – 250
Column temp.: 25 °C
Eluent: 2, 3, 4, 5, 6 and 7 mmol/L Na_2CO_3
15, 20, 25 and 30 mmol/L NaOH
Flow: 0.8 mL/min
Loop: 20 µL

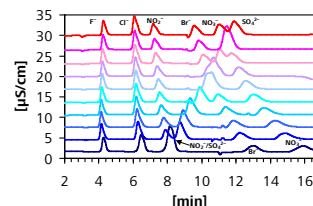


Increasing the eluent concentration of NaOH improves the separation of the nitrate and sulfate peak. However, a too high NaOH concentration shortens retention times and thus affects separation.

→ An eluent consisting of 3...4 mmol/L Na_2CO_3 and 25 mmol/L NaOH is ideal.

Column temperature

Column: Metrosep A Supp 16 – 250
Column temp.: 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60 °C
Eluent: 3 mmol/L Na_2CO_3
25 mmol/L NaOH
Flow: 0.8 mL/min
Loop: 20 µL



Decreasing temperature

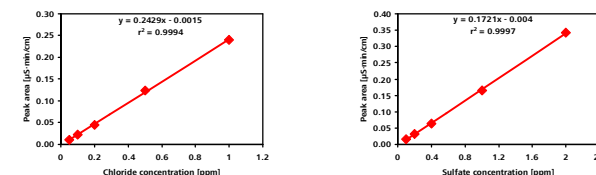
- only marginally influences the retention times of fluoride and chloride
- increases retention times of nitrite, bromide and nitrate
- decreases retention times of sulfate

On the one hand lower column temperatures favor the chromatographic separation of the chloride, sulfate and the nitrate peak. On the other hand nitrite and sulfate coelute at very low temperature (15 °C).

→ A column temperature of 25 °C guarantees an excellent separation of all anions.

Data evaluation

Calibration



	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5	
	Peak area · 10	Concentration	Peak area · 10	Concentration	Peak area · 10	Concentration
Chloride	0.11122	0.05	0.22950	0.10	0.44230	0.20
Sulfate	0.15234	0.10	0.31466	0.20	0.63400	0.40
	1.23655	0.50	1.64721	1.00	3.41942	2.00
						Coefficient of determination
						0.9994
						0.9997

Peak areas in $\mu\text{S}\cdot\text{min}\cdot\text{cm}^{-1}$, concentrations in ppm

Spike recovery

The recovery rate of the spiked chloride and sulfate is a measure for the accuracy of the method. At first two different diluted nitric acid (1:100, w/w) samples were analyzed. Afterwards the nitric acid samples were spiked with two different chloride (0.1 and 0.2 ppm) and sulfate (0.2 and 0.4 ppm) concentrations, respectively.

	Chloride			Sulfate		
	spike [ppm]	Conc.¹ [ppm]	Recovery [%]	spike [ppm]	Conc.¹ [ppm]	Recovery [%]
HNO_3^2	—	0.0519	—	—	0.1849	—
HNO_3^2 + spike 1	0.1	0.1534	101.47	0.2	0.3864	100.77
HNO_3^2 + spike 2	0.2	0.2552	101.61	0.4	0.6088	105.97

¹mean of four determinations, ²1:100 (w/w) diluted

Spike recovery rates for chloride and sulfate ranged between 95...102% and 95...106%, respectively. Chloride concentrations in the two undiluted nitric acid samples were 5.19 and 2.93 ppm; sulfate concentrations 18.49 and 5.1 ppm, respectively.

Sample 2 + spike 2

Spike conc.: 0.2 ppm chloride
0.4 ppm sulfate

Column: Metrosep A Supp 16 – 250
Column temp.: 25 °C

Eluent: 3 mmol/L Na_2CO_3
25 mmol/L NaOH

Flow: 0.8 mL/min
Loop: 20 µL

