Determination of pyrophosphate, trimetaphosphate, tripolyphosphate and standard ions in detergents or fertilizers using IC with a high-capacity suppressor

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Metrohm Ion analysis

Ion Chromatography

Summary

This paper describes the separation and determination of phosphates in the presence of monovalent and/or divalent anions by direct injection suppressed ion chromatography. Depending on the particular separation problem the isocratic or gradient mode was applied.

Divalent anions such as sulfate and citrate can be determined in a single run together with ortho- (PO_4^{3-}), pyro- ($P_2O_7^{4-}$), trimeta- ($P_3O_9^{3-}$) and tripolyphosphate ($P_3O_{10}^{5-}$) under isocratic conditions using either the 828 IC Dual Suppressor (chemical plus CO_2 suppression) or the high-capacity suppressor. While the first one with its extremely low background conductivity yields excellent sensitivity for early eluting peaks, the XL Suppressor with subsequent CO_2 suppression excels in a high sensitivity for stronger retained phosphates.

The presented gradient IC separation allows the simultaneous identification and determination of monovalent ions such as fluoride, chloride, bromide and nitrate in the presence of sulfate and the above-mentioned phosphates.

Introduction

In the environment, phosphates are often limiting the growth rate of organisms. However, the increasing use of phosphates in detergents and fertilizers has significantly influenced its bioavailability, leading to an unbalanced growth of some organisms at the expense of others.

Because of the important role phosphate species play in biochemical systems and in industrial applications, highly efficient monitoring tools are needed. In contrast to the time-consuming and tedious wet-chemical methods, ion chromatography (IC) offers sensitive and straightforward analyses of phosphate species.

Three different suppressor systems, the 828 IC Dual Suppressor and the XL Suppressor with and without subsequent CO_2 suppression are compared in terms of sensitivity.

Additionally, binary gradient elution was applied to analyze phosphates besides the mono- and divalent ions.

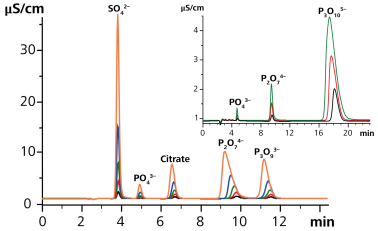
System setup

- 820 IC Separation Center
- 819 Advanced IC Detector
- 818 Advanced IC Pump
- 830 Advanced IC Interface
- 838 Advanced IC Sample Processor
- 828 IC Dual Suppressor
- 853 CO_2 Suppressor – «MCS»
- 833 Advanced IC Liquid Handling XL Suppressor

Isocratic elution

828 IC Dual Suppressor

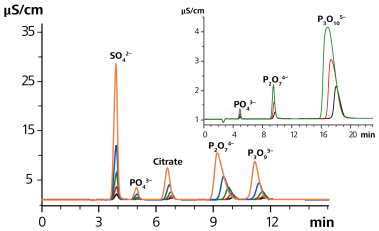
Column: A Supp 5 – 100
Eluent: 40 mmol/L NaOH
Flow: 0.7 mL/min
Loop: 20 µL



Since the tripolyphosphate standard contained impurities of orthophosphate and pyrophosphate, the calibration of the tripolyphosphate anion was performed in a separate chromatographic run. The analytical unit provided an excellent baseline separation of sulfate, citrate and the phosphates.

XL Suppressor with CO_2 Suppressor

Column: A Supp 5 – 150
Eluent: 40 mmol/L NaOH
Flow: 0.7 mL/min
Loop: 20 µL



The exchange of the 828 IC Dual Suppressor against the XL Suppressor and the 853 CO_2 Suppressor resulted in a smaller peak height for sulfate.

Comparison

For comparison of the chromatographic performance, resulting peak areas and heights of calibration standards were utilized. Peak areas and heights are indicated in % and are all referenced to the results with the XL and CO_2 Suppressor.

	828 Dual Suppressor Peak area [%]	828 Dual Suppressor Peak height [%]	XL Suppressor with CO_2 Suppressor Peak area [%]	XL Suppressor with CO_2 Suppressor Peak height [%]	XL Suppressor Peak area [%]	XL Suppressor Peak height [%]
Sulfate[1]	96	135	100	100	84	90
Orthophosphate[1]	88	115	100	100	74	80
Citrate[1]	91	108	100	100	60	66
Pyrophosphate[1]	94	96	100	100	74	81
Trimetaphosphate[1]	89	100	100	100	73	80
Tripolyphosphate[2]	93	75	100	100	106	74
Background cond. [µS/cm]	0.98		1.02		3.15	

[1]mean of five determinations; [2]mean of three determinations

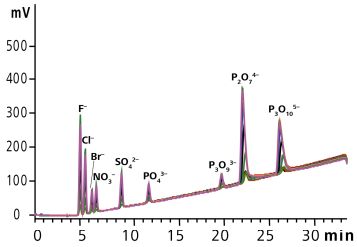
While the XL Suppressor in combination with the CO_2 Suppressor provides the highest peak areas, the 828 IC Dual Suppressor yields, especially for the early eluting peaks, the best peak heights. Without the CO_2 Suppressor both peak areas and peak heights are smaller, due to the higher residual CO_2 concentrations after suppression.

Gradient elution

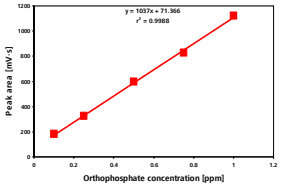
The presented suppression techniques have significantly reduced the injection peak and the background conductivity, thus allowing for a simple and sensitive detection of early eluting anions. However, the presence of halides in the sample leads to coelution with sulfate and/or orthophosphate and thus requires a gradient elution.

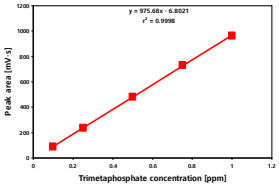
Column: Metrosep A Supp 3 – 250
Eluent A: Ultrapure water
Eluent B: 40 mmol/L NaOH
Flow: 1.0 mL/min
Loop: 20 µL
Gradient:

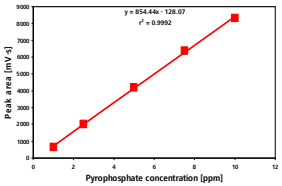
0.0 min	85% A	15% B
15.0 min	60% A	40% B
30.0 min	30% A	70% B
30.1 min	85% A	15% B
35.0 min	85% A	15% B

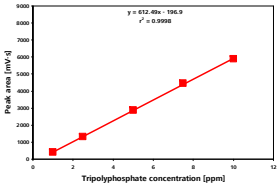


Calibration









	Standard 1 Peak area[1]	Standard 1 Concentration	Standard 2 Peak area[1]	Standard 2 Concentration	Standard 3 Peak area[1]	Standard 3 Concentration	Standard 4 Peak area[1]	Standard 4 Concentration	Standard 5 Peak area[1]	Standard 5 Concentration	Coefficient of determination
Fluoride	348.13		931.13		1978.15		3073.29		4089.88		0.9998
Chloride	233.34		611.09		1396.26		–		2659.95		0.9980
Bromide	89.44		218.07		444.50		675.56		902.54		0.9999
Nitrate	103.74	0.10	263.53	0.25	546.65	0.50	829.72	0.75	1110.36	1.00	0.9999
Sulfate	177.60		439.47		899.80		1351.98		1792.92		0.9999
Orthophosphate	180.12		327.07		596.44		828.41		1120.99		0.9988
Trimetaphosphate	89.71		235.52		481.89		731.85		963.79		0.9998
Pyrophosphate	658.02	1.00	2011.63	2.50	4208.90	5.00	6385.87	7.50	8310.59	10.00	0.9992
Tripolyphosphate	421.02		1306.92		2872.35		4445.77		5894.12		0.9998

[1]mean of three determinations; peak areas in mV·s, concentrations in ppm

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