Analysis of produced water contaminants by ion chromatography

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Metrohm
Ion analysis

Ion Chromatography

Summary

The analytical challenge treated by the present work consists in detecting sub-ppm quantities of bromide, sulfate, aliphatic monocarboxylic acids and several alkaline earth metals in the presence of very high concentrations of sodium and chloride. Bromide, sulfate, acetate and butyrate can reliably be determined by suppressed conductivity detection. Due to matrix effects, propionate can only be detected qualitatively. This drawback can be overcome by coupling the ion chromatograph (IC) to a mass spectrometric (MS) detector. This results in reduced matrix interferences and significantly enhanced sensitivities.

The cations magnesium, barium and strontium are determined by non-suppressed conductivity detection.

Introduction

Produced water is water trapped in underground reservoir rocks that is brought to the surface along with the crude oil and gas. Besides dispersed oil droplets and dissolved organic compounds, produced water mainly contains significant amounts of inorganic cations such as calcium, magnesium, barium and strontium, and anions such as carbonate, bromide and sulfate. Precipitation of the corresponding salts often leads to the formation of scale deposits that can clog pipes.

For these reasons it is of paramount importance to determine the inorganic constituents of produced water, not least for determining the correct dosing of scale inhibitors. Additionally, the detection of dissolved organic acids is of particular interest as they indicate the presence of oil.

Of the numerous analytical techniques for the determination of ionic species, ion chromatography (IC) is the best suited in terms of selectivity, flexibility, automation and ruggedness. This poster presents an overview of the different IC-based methods used for determining ionic components in produced water.

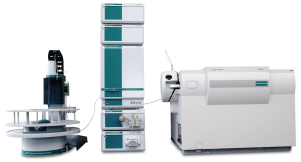
IC/MS

- 818 Advanced IC Pump
- 819 Advanced IC Detector
- 820 IC Separation Center
- 830 Advanced IC Interface
- 833 Advanced IC Liquid Handling Pump Unit
- 838 Advanced IC Sample Processor
- 1100 MSD SL, Agilent Technologies

Conductivity detection

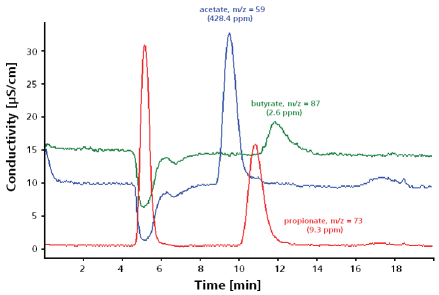
- 850 Professional IC Anion – MCS
- 858 Professional Sample Processor – Pump

Alternatively, all analyses can be performed with the 861 Advanced Compact IC.



Aliphatic monocarboxylic acids

a) IC/MS

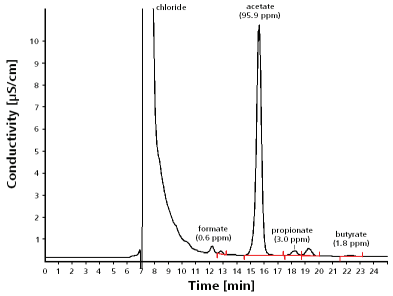


Anion exclusion chromatography with MS detection after post-column (PC) addition of ammonia

Sample prep.:	1:10 dilution, dialysis	**PC solution:**	300 mmol/L ammonia
Column:	Metrosep Organic Acids – 100	**ESI:**	13 L/min N_2, 350 °C, 60 psig, 3 kV
Eluent:	0.25 mmol/L oxalic acid	**MSD:**	SIM neg.
Flow:	0.4 mL/min	**Fragmentor:**	70 V
Loop:	10 µL		

Matrix interferences are reduced to an absolute minimum and carboxylic acids can be sensitively determined even in the presence of high salt concentrations.

b) Conductivity detection

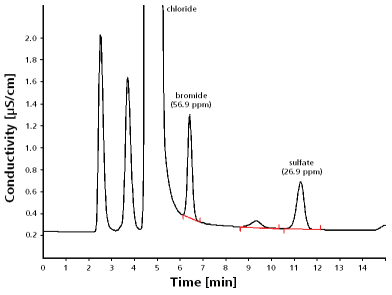


Anion exclusion chromatography with suppressed conductivity detection

Sample prep.:	1:5 dilution, acidification with 0.05 mmol/L sulfuric acid	**Eluent:**	0.5 mmol/L sulfuric acid
		Flow:	0.5 mL/min
Column:	Metrosep Organic Acids – 250	**Loop:**	100 µL
Precolumn:	Metrosep RP Guard		

Target compounds are well separated from the chloride peak.

Bromide and sulfate

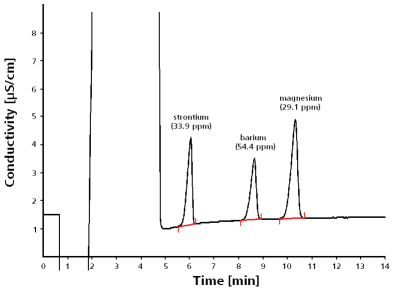


Anion exchange chromatography with suppressed conductivity detection

Sample prep.:	Ultrasonic treatment for 10 minutes, filtration through a 0.45 µm filter, 1:20 dilution	**Eluent:**	1.8/1.7 mmol/L Na_2CO_3/$NaHCO_3$
		Flow:	1.0 mL/min
		Loop:	20 µL
Column:	Metrosep A Supp 4 – 250		
Precolumn:	Metrosep RP Guard		

Despite the high chloride concentration in process water samples, bromide and sulfate can be accurately determined.

Magnesium, barium and strontium



Cation exchange chromatography with direct conductivity detection

Sample prep.:	Ultrasonic treatment for 10 minutes, filtration through a 0.45 µm filter, acidification with nitric acid to a pH of 2.5	**Eluent:**	4.0 mmol/L tartaric acid 3.0 mmol/L ethylene diamine 0.5 mmol/L dipicolinic acid + 5% acetone
Column:	Nucleosil 5SA		
Precolumn:	Metrosep RP Guard	**Flow:**	1.5 mL/min
		Loop:	20 µL

Since the monovalent cations elute with the injection peak, even high sodium concentrations do not interfere with the determination of low concentrated alkaline earth metal concentrations.

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