Ion chromatographic determinations of anions, cations and organic acids in biofuels

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Metrohm Ion analysis

Ion Chromatography

Introduction

The reduction of the greenhouse gas emissions and the assessment of renewable energy sources are among today's most challenging tasks. In this context biofuels such as biodiesel, bioethanol and biogas have emerged as promising alternatives. However, successful commercialization and market acceptance of biofuels were retarded by reports highlighting the presence of ions that induce corrosion in the vehicle components and salt deposits that clog filters and fuel injector nozzles. Therefore, standards defining quality specifications and test methods have been developed. In this context ion chromatography (IC) plays a decisive role. Besides the quantitation of cations, glycerol and antioxidants in biodiesel, a direct-injection IC method allows the determination of the chloride and sulfate content in bioethanol according to the recent ASTM D 4806 standard.

In addition, IC has become an invaluable tool for the process control and monitoring of biogas reactor samples. The anaerobic digestion is a multistage microbial process. Before symbiotic groups of bacteria transform complex organic waste material to biogas, hydrolytic and fermentative bacteria have to convert the waste, producing primarily low-molecular-weight organic acids. Under steady-state conditions these acids are buffered by the digestion matrix (lime, carbonates) and the pH is kept above the critical value of 6.5. However, due to poor feedstock quality or high loading rates, the production of organic acids can exceed the slurry's buffer capacity. Consequently, methanogenesis and acetogenesis can be retarded or even stop completely. Concentration profiles of the carboxylic acids thus provide important information regarding the progress of the reaction. However, unlike the above-mentioned direct-injection IC, the analysis of a complex anaerobic digestion matrix requires efficient matrix elimination steps.

This poster provides an overview of ion chromatographic methods combined with inline sample preparation for the determination of anions and cations in organic biofuels and volatile organic acids in process solutions.

Instrumentation

Anions in an ethanol/gasoline blend

- 818 Advanced IC Pump
- 819 Advanced IC Detector
- 820 IC Separation Center
- 830 Advanced IC Interface
- 833 Advanced IC Liquid Handling Suppressor
- 838 Advanced IC Sample Processor
- 853 CO_2 Suppressor – «MCS»
- Metrosep A PCC 1 HC

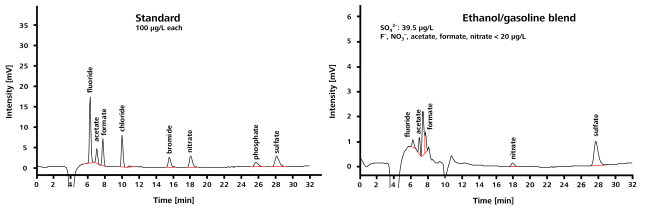
Cations in biodiesel

- 861 Compact IC
- 833 Advanced IC Liquid Handling Dialysis Unit
- 833 Advanced Liquid Handling Pump Unit
- 772 Pump Unit
- 838 Advanced IC Sample Processor
- 800 Dosino

Organic acids in biogas reactor samples

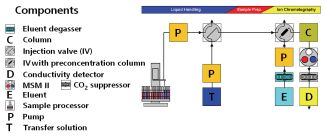
- 861 Compact IC
- 833 Advanced IC Liquid Handling Dialysis Unit
- 833 Advanced Liquid Handling Pump Unit
- 838 Advanced IC Sample Processor

Anions in an ethanol/gasoline blend (E85)



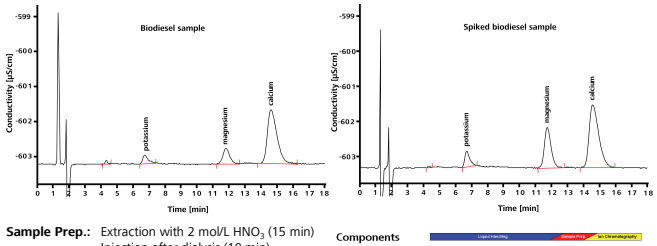
Sample Prep.:	Matrix elimination
Column:	Metrosep A Supp 7 – 250
Eluent:	3.6 mmol/L Na_2CO_3 7.5% acetone in ultrapure water
Flow:	0.8 mL/min
Loop:	10 µL
Transfer sol.:	7.5% acetone in ultrapure water

Components



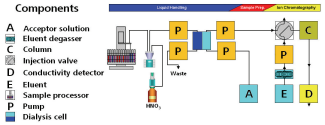
While the organic ethanol/gasoline blend is washed away, the analyte ions are retained on the preconcentration column.

Cations in biodiesel



Sample Prep.:	Extraction with 2 mol/L HNO_3 (15 min) Injection after dialysis (10 min)
Column:	Metrosep C 2 – 150
Eluent:	2 mmol/L HNO_3 10% acetone in ultrapure water
Flow:	1.0 mL/min
Loop:	20 µL

Components

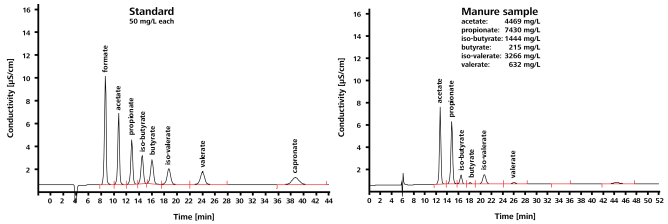


The continuous flow-through dialysis cell can be directly connected to the injection valve of the IC instrument.

	Concentration				Spike recovery
	Sample [mg/L]	Spike [mg/L]	Theoretical [mg/L]	Measured [mg/L]	[%]
Potassium	1.156	1.0	2.156	2.039	94.57
Magnesium	0.749	1.0	1.749	1.694	96.86
Calcium	4.977	1.0	5.977	5.822	97.41

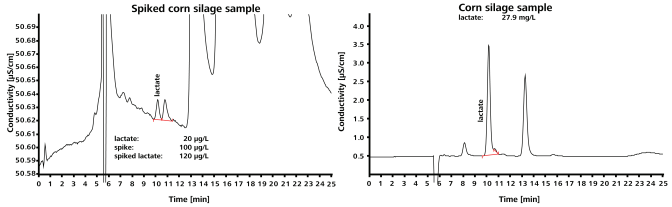
Organic acids in biogas reactor samples

a) Liquid manure



Sample Prep.:	1:100 dilution with ultrapure water injection after dialysis (10 min)	**Flow:**	0.6 mL/min
Column:	Metrosep Organic Acids 250	**Loop:**	20 µL
Eluent:	0.5 mmol/L $HClO_4$		

b) Corn silage



In contrast to the manure sample, the silage samples were diluted 1:50 and subsequently filtrated. The other experimental conditions were kept constant.

Summary

Quality and process control of biofuels require straightforward, fast and accurate analysis methods. Ion chromatography (IC) is at the leading edge of this effort.

Traces of anions in a gasoline/ethanol blend can accurately be determined in the sub-ppb range after Metrohm Inline Matrix Elimination using anion chromatography with conductivity detection after sequential suppression. While the analyte anions are retained on the preconcentration column, the interfering organic gasoline/bioethanol matrix is washed away.

Detrimental alkali metals and water-extractable alkaline earth metals in biodiesel are determined in the sub-ppm range using cation chromatography with direct conductivity detection applying automated extraction with nitric acid and subsequent Metrohm Inline Dialysis. Unlike high-molecular substances, ions in the high-ionic strength matrix diffuse through a membrane into the low-ionic water acceptor solution.

In biogas reactor samples, low-molecular-weight organic acids stem from the biodegradation of organic matter. Their profile allows important conclusions concerning the conversion of the anaerobic digestion reaction. Volatile fatty acids and lactate can be accurately determined applying ion exclusion chromatography with suppressed conductivity detection after inline dialysis or filtration.

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