# Quality assurance of biofuels

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Ion Chromatography


## Summary

Quality and process control of biofuels both require straightforward, fast and accurate analysis methods. Ion chromatography (IC) is perfectly able to meet this challenge.

Traces of anions in a gasoline/ethanol blend can be accurately 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/ethanol matrix is washed away.

After automated extraction with nitric acid and subsequent Metrohm Inline Dialysis, the 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. Unlike high-molecular substances, ions in the high-ionic strength matrix diffuse through a membrane into the low-ionic water acceptor solution.

The 873 Biodiesel Rancimat allows the convenient and reliable determination of the oxidation stability. The increased temperature accelerates the oxidation of the biodiesel, leading to the formation of low-molecular organic acids. These are transferred by the air stream to a second vessel containing distilled water. The conductivity in this vessel is recorded continuously to detect the organic acids. The time that elapses until these secondary reaction products appear is called oxidation stability, induction time or induction period and characterizes the resistance of biodiesel against oxidation. The standardized test is described by the European Standard EN 14112 «Fat and oil derivatives – Fatty acid methyl esters (FAME) – Determination of oxidation stability (accelerated oxidation test)».


## Introduction

The reduction of the greenhouse gas emissions and the assessment of renewable energy sources are among the most challenging tasks of our time. In this context biofuels such as biodiesel, bioethanol and biogas have emerged as promising alternatives. However, the successful commercialization and market acceptance of biofuels have been retarded by reports highlighting the presence of ions that induce corrosion in the vehicle components in contact with fuel and salt deposits that clog filters and fuel injector nozzles. Therefore, standards defining quality specifications and test methods have been developed.

Besides the ion chromatographic (IC) methods for the quantitation of water-extractable cations, glycerol and antioxidants in biodiesel, there is a direct-injection IC method that allows the determination of the chloride and sulfate content in bioethanol according to the ASTM standard D 4806. Alternatively, Metrohm`s Inline Matrix Elimination allows to concentrate the target anions on a preconcentration column, the organic matrix being flushed to waste.

Oxidation stability (aging behavior) is the parameter that characterizes the resistance against fuel oxidation. Sufficient oxidation stability is an indispensable prerequisite for a failure-free operation of the fuel injection equipment. The European Standard EN 14112 describes the standardized test, which can be reliably carried out with the 873 Biodiesel Rancimat.

| BIODIESEL<br>Property | Test method | Limits<br>EN 14214 | <br>EN 14213 | Test method | Limits<br>ASTM D 6751 |
|---|---|---|---|---|---|
| **Oxidative stability, 110 °C [h]** | EN 14112 | ≥6 | ≥4 | EN 14112 | ≥3 |
| **Group I metals (Na + K) [mg/kg]** | EN 14108<br>EN 14109 | ≤5 | – | EN 14538 | ≤5 |
| **Group II metals (Ca + Mg) [mg/kg]** | EN 14538 | ≤5 | – | EN 14538 | ≤5 |
| **Total glycerol [% mass]** | EN 14105 | ≤0.25 | – | ASTM D 6584 | ≤0.24 |
| **BIOETHANOL**<br>**Property** | | **Limits**<br>**ASTM D 4806** | **ASTM D 5798** | | **EN 15376** |
| **Inorganic chloride [mg/L]** | ASTM D 512 | ≤40 | ≤1 | EN 15484$_{Pot}$<br>EN 15492$_{IC}$ | ≤20 |
| **Inorganic sulfate [mg/L]** | ASTM D 7318$_{Pot}$<br>ASTM D 7319$_{IC}$[a]<br>ASTM D 7328$_{IC}$[b] | ≤4 | – | EN 15492$_{IC}$ | –[c] |

[a]direct injection of the denaturated fuel ethanol
[b]injection of the sample after complete evaporation of the ethanol sample and dissolving in
- water (total sulfate) or in
- 1% aqueous hydrogen peroxide solution (so-called potential sulfate)
[c]the limit value for the highest acceptable sulfate concentration will be evaluated in the revised EN 15492

This poster provides an overview of ion chromatographic methods combined with inline sample preparation for the determination of anions and water-extractable cations in biofuels. In addition, the determination of the oxidation stability is described.

## Instrumentation

**Anions in an E85 blend**

- 881 Compact IC pro – Anion
- 858 Professional Sample Processor – Pump – Injector

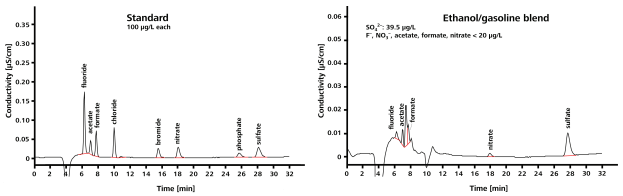
**Cations in biodiesel**

- 850 Professional IC system with inline dilution and dialysis

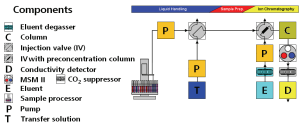
**Oxidative stability of biodiesel**

- 873 Biodiesel Rancimat

## Anions in an ethanol/gasoline blend (E85)

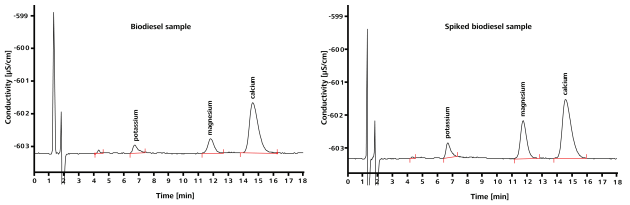



**Sample Prep.:** Matrix elimination
**Column:** Metrosep A Supp 7 – 250
**Eluent:** 3.6 mmol/L $Na_2CO_3$
7.5% acetone in ultrapure water
**Flow:** 0.8 mL/min
**Loop:** 10 µL
**Transfer sol.:** 7.5% acetone in ultrapure water

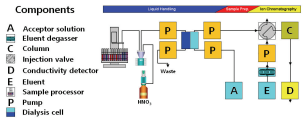



While the organic ethanol/gasoline blend is washed away, the analyte ions are retained on the preconcentration column.

## Cations in biodiesel



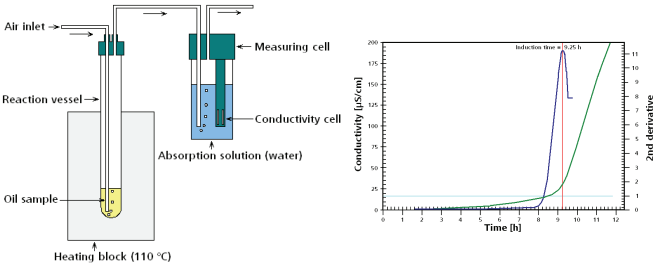

**Sample Prep.:** Extraction with 2 mol/L $HNO_3$ (15 min)
Injection after dialysis (10 min)
**Column:** Metrosep C 4 – 150
**Eluent:** 2 mmol/L $HNO_3$
10% acetone in ultrapure water
**Flow:** 1.0 mL/min
**Loop:** 20 µL




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

| | Concentration | | | | Spike recovery |
|---|---|---|---|---|---|
| | Sample | Spike | Theoretical | Measured | |
| | [mg/L] | [mg/L] | [mg/L] | [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 |

## Oxidation stability of biodiesel




At 110 °C the investigated biodiesel sample has an induction time of 9.25 h. It thus complies with the minimal requirements of EN 14112 in EN 14214 (6 h) and ASTM 6751 (3 h).

## References


(1) G. Knothe, Analyzing biodiesel: standards and other methods, JAOCS **83**(10), 823-833 (2006).
(2) A. Steinbach, U. Loyall, B. Zumbrägel, C. Haider, G. Spinnler, R. Schlink and A. Wille, Quality control of biofuels, Biofuels plant & technology – Supplement to PTQ (2008).
(3) C. Haider and G. Spinnler, Titrimetric analysis of biofuels, Pittcon 2008, http://products.metrohm.com (search for 8.000.6020EN).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