

Biofuel Analysis by Ion Chromatography

Alfred Steinbach,¹ Andrea Wille¹ and N. Harihara Subramanian,²

¹Metrohm AG, Herisau, Switzerland,

²Micro Devices Metrohm Ltd, Chennai, India.

Introduction

The four primary driving forces behind biofuels are the world's increasing thirst for petroleum (80 Mbarrels/day), the diminishing supply of fossil fuels, global warming and the intention to reduce the dependence on fuel imports. Additionally, most biofuels are produced by straightforward manufacturing processes, are readily biodegradable and nontoxic, have low emission profiles and can be used as is or blended with conventional fuels. At this time biodiesel and bioethanol are the leading fuel alternatives, driven by recent regulations such as the US Department of Energy's Federal Biobased Products Preferred Procurement Program (FB4P) or the EU Directive 2003/30/EC.

The concept of using liquid biofuel dates back to the year 1895 when the German engineer Rudolf Diesel (1858–1913) developed the first engine running on vegetable oil. The motors of that time with their large injectors could easily cope with viscous vegetable fuels. However, as a result of the low petroleum prices, engine technology was increasingly tailored to consume low-viscosity conventional fuel. Consequently, vegetable oils were only sought after in times of high oil prices.

It was not until vegetable oils were derivatized that low-viscosity biofuel was available. In a reaction that is catalysed by a base, acid or enzyme, a vegetable oil or animal fat is reacted with methanol to yield fatty acid methyl esters (FAME, biodiesel) and glycerol as by-product. The latter, if produced in high quality, finds use as a valuable feedstock in the cosmetic and pharmaceutical industry. The base-catalysed transesterification is considered as the most promising production process (Figure 1).¹

As a result of the reversible character of the reaction, a large excess of alcohol shifts the equilibrium to the products side and thus ensures total conversion to the esters. After completion of the transesterification reaction, the biodiesel phase is separated from the more dense glycerol phase by gravitational settling or centrifugation. Subsequently the methyl esters, which still contain large amounts of residual alcohol, traces of dispersed glycerol and unreacted sodium hydroxide or soaps, are cleaned by a water-wash. Remaining water and poorly water-soluble impurities, such as the unreacted feedstock or the mono- and diglycerides, are removed by further steps such as distillation or stripping.

In 1908, some years after the development of the diesel engine, Henry Ford (1863–1947) designed the Ford Model T to run on ethanol. However, the low petroleum prices and the seemingly inexhaustible fossil fuel reserves also displaced the ethanol. It was not until the worldwide oil crisis in 1973 that Brazil and the US launched their first ethanol programmes and thus paved the way for their actual leadership position concerning production and use of bioethanol.

Generally, bioethanol is made from products containing sugar, starch or lignocellulosic biomass. The microbial fermentation of biomass-sourced sugars via yeast is a well established technology that is applied commercially on a large scale. In contrast, starch biomass with its larger carbohydrates is not directly fermentable. Prior to yeast-induced fermentation, starch-containing feedstock has to be converted to sugars. Fermentation yields relatively dilute aqueous solutions of ethanol, that, for their later use as a fuel, are distilled to provide 95% ethanol. The "anhydrous" 99% ethanol is mainly produced via physical water absorption by molecular sieve.

Despite all the advantages mentioned at the beginning of this paper, biofuels had to struggle for acceptance right from the start. Reports highlighting engine problems because of poor quality biofuel discredited the promising biogenic route. Low-quality biodiesel, often produced from crude feedstocks in uncontrolled home-brewing plants, contained detrimental contaminants, resulting in injector fouling, enhanced corrosion and clogging of the fuel system. Not until reliable quality standards were defined did the quality of biofuels and thus the

Figure 1: Base-catalysed transesterification of a triacylglyceride with methanol.

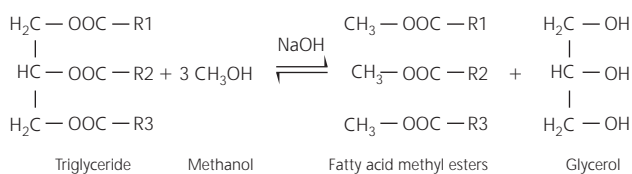
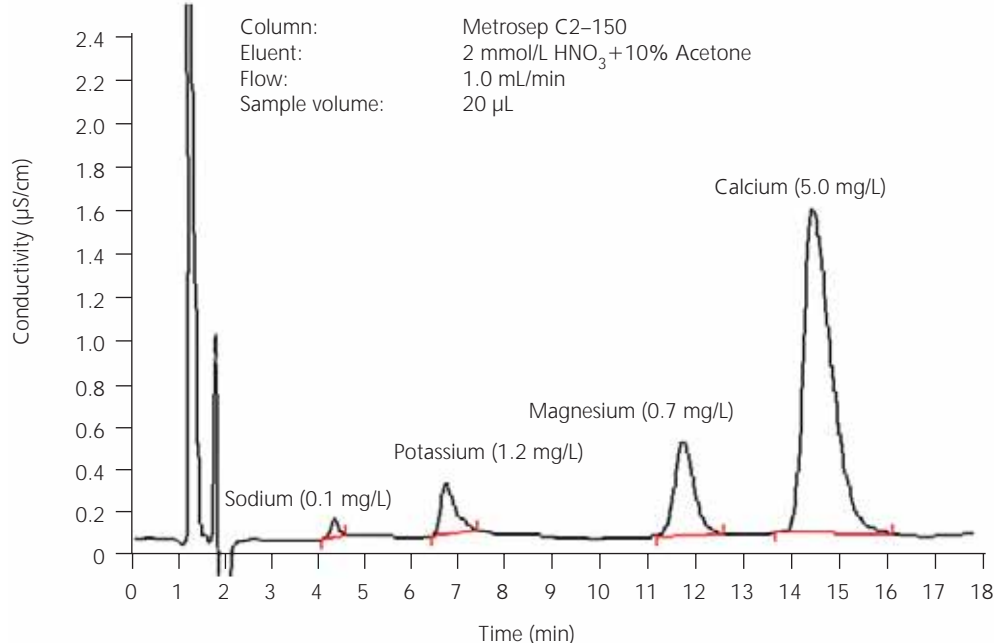


Table 1(a): European and US biodiesel standards (selection).

BIODIESEL	EN 14214/14213	EN 14214	EN 14213	ASTM D 6751	
Property	Test method	Limits		Test method	Limits
Group I metals (Na + K) (mg/kg)	EN 14108 EN 14109	< 5.0	—	EN 14538	< 5.0
Group II metals (Ca + Mg) (mg/kg)	EN 14538	< 5.0	—	EN 14538	< 5.0
Total glycerol (% mass)	EN 14105	< 0.25	—	ASTM D 6584	< 0.24

Table 1(b): US and European biodiesel standards (selection).

BIOETHANOL Property	ASTM D 4806 ASTM D 5798		prEN 15376	
	Test method	Limits	Test method	Limits
Inorganic chloride (mg/L)	ASTM D 512	< 40 < 1	prEN 15484 prEN 15492	< 20
Inorganic sulphate (mg/L)	ASTM D 7318 _{pot} ASTM D 7319C	< 4	—	—

Figure 2: Separation and detection of alkali metals and alkaline earth metals.

confidence of the consumer and the automobile industry improve. The major biodiesel standards, which commonly serve as reference for other standards, are the ASTM D 6751 from the American Society for Testing and Materials and the European EN 14214 [Table 1(a)]. Additionally, there exists the separate standard EN 14213 defining the minimal requirements for biodiesel used as heating oil or as a blending component for heating oil.

On the one hand these standards include fuel-inherent properties such as the oxidation stability or the iodine value. These so-called structure indices originally served to exclude the use of certain vegetable oils or animal fats as feedstocks.² On the other hand there are properties that are basically related to the production process. These parameters, also called quality indices, indicate the content of unreacted starting material in the biodiesel. Process-related parameters comprise the acid number as well as the glycerol, methanol, water and sodium hydroxide content.

While the standardization of biodiesel in Europe has been well established by the EN 14214 since 2003, the European standard for bioethanol, the prEN 15376 is currently under approval. In contrast, the leading ethanol producers, the US and Brazil, adhere to two well-established standards, the ASTM D 4806 and

the ASTM D 5798 for denatured fuel ethanol only and for mixtures of bioethanol and gasoline (Ed75-Ed85), respectively [Table 1(b)].

This article provides an overview of straightforward ion chromatographic methods for the simple and accurate determination of alkali metals, alkaline earth metals, antioxidants as well as chloride and sulphate in biofuels. The description of the ion chromatographic analysis of free and total glycerol is beyond the scope of this article and will be published at a later date.

Experimental

Instrumentation

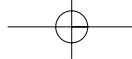
Separation columns and main instrumental parameters are listed in the corresponding chromatograms. Instrument control, data acquisition and processing were done by IC Net and MagIC Net software (Metrohm AG). The following analytical systems were used:

(a) Alkali metal and alkaline earth metal determination

861 Advanced Compact IC

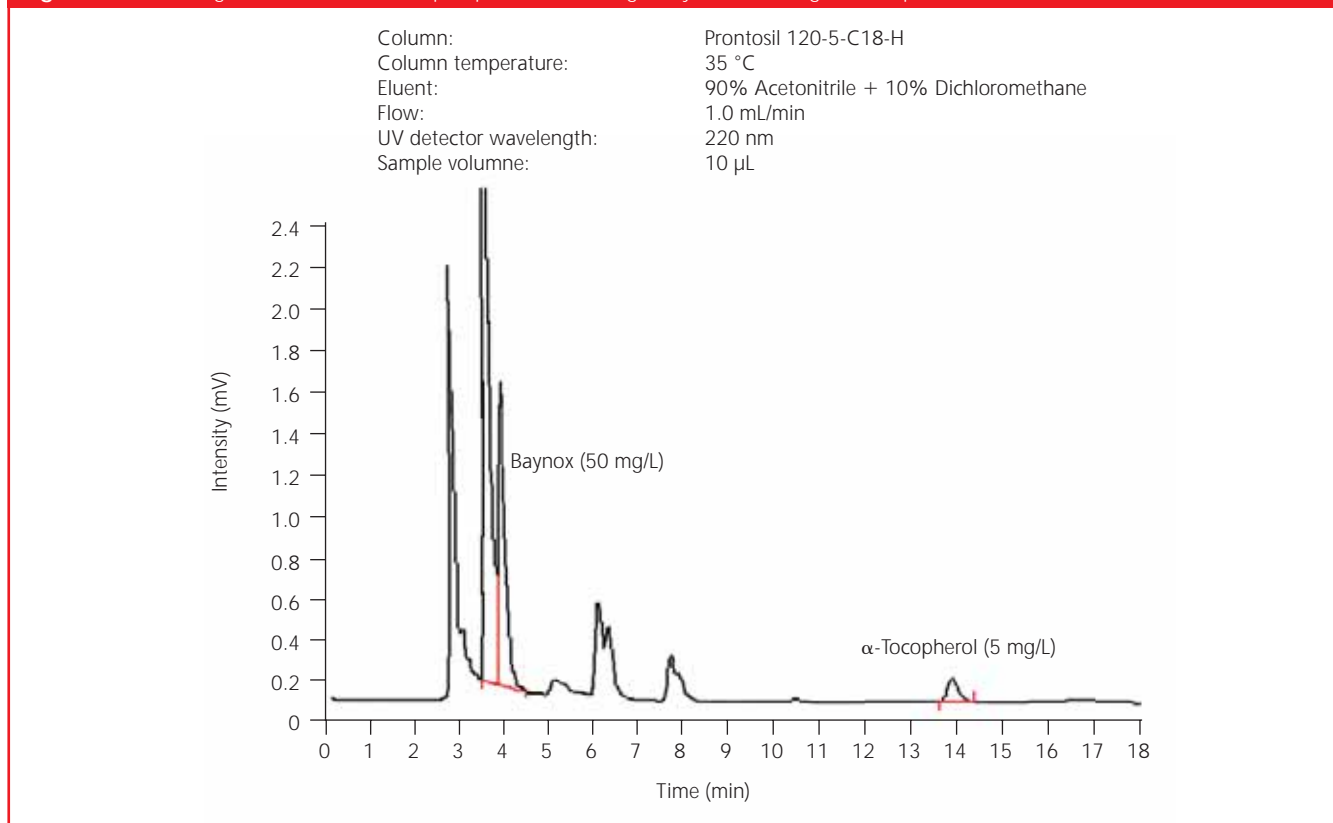
838 Advanced IC Dilution Sample Processor

833 Advanced IC Liquid Handling Dialysis Unit



General

Figure 3: Chromatogram of a biodiesel sample spiked with 50 mg/L Baynox and 5 mg/L α -tocopherol.



(b) Antioxidant determination

844 UV/VIS Compact IC
838 Advanced IC Sample Processor

(c) Chloride and sulphate determination

850 Professional IC Anion — MCS
858 Professional Sample Processor — Pump.

Standard solutions and eluents

All reagents used in this work were of the highest purity grade (puriss p.a.). Alkali metal, alkaline earth metal, chloride, sulphate and α -tocopherol standards were all purchased from Fluka (Sigma-Aldrich, Buchs, Switzerland). Baynox was purchased from Lanxess (Leverkusen, Germany). All solutions were prepared with deionized water with a specific resistance higher than 18 M Ω cm.

(a) Alkali Metals and Alkaline Earth Metals in Biodiesel

After transesterification and subsequent treatment, alkali metals and alkaline earth metals may be present in biodiesel as unwanted residues. While sodium and potassium contaminations stem from the use of the corresponding hydroxides in the transesterification reaction, calcium and magnesium contaminations derive from the use of hard water to extract impurities or from the use of certain adsorbents to remove them. Standard DIN EN 14 214 permits a cumulative concentration of 5 mg/kg for both the alkali metals sodium and potassium and also for the alkaline earth metals magnesium and calcium. Both groups of cations can be determined rapidly and accurately in a single ion chromatographic run (Figure 2).

Sample preparation

The samples are extracted with dilute nitric acid, dialysed and then injected directly into the IC system.³ The complete sample preparation procedure and analysis takes place fully automatically (Metrohm inline extraction and dialysis).

(b) Antioxidants in Biodiesel

The oxidation stability of biodiesel can be improved by the addition of antioxidants. The addition of Baynox to the biodiesel sample inhibits both the oxidation to corrosive acids and the formation of insoluble polymers. Although not regulated by standards, these substances are determined within the context of quality monitoring and for determining the amounts of additives to be added.

Sample preparation

Because of their structural similarities, α -tocopherol (vitamin E) and Baynox can be determined together in a single analysis (Figure 3). To improve solubility, dichloromethane is added to the eluent and analyte solutions. The biodiesel samples should be diluted 1:1000. The analytes are separated at 35 °C and determined quantitatively using UV detection. The method can be completely automated with the 838 Advanced IC Sample Processor.

(c) Chloride and Sulphate in Ethanol

Contamination of ethanol with inorganic anions such as chloride and sulphate can affect the engine performance because precipitating salts clog filters and fuel injector nozzles. Furthermore, these salts induce corrosion in the vehicle components in contact with the fuel. Against this background, the ethanol specification ASTM D 4806 limits the sulphate and chloride content to 4 and 40 mg/L, respectively.

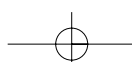
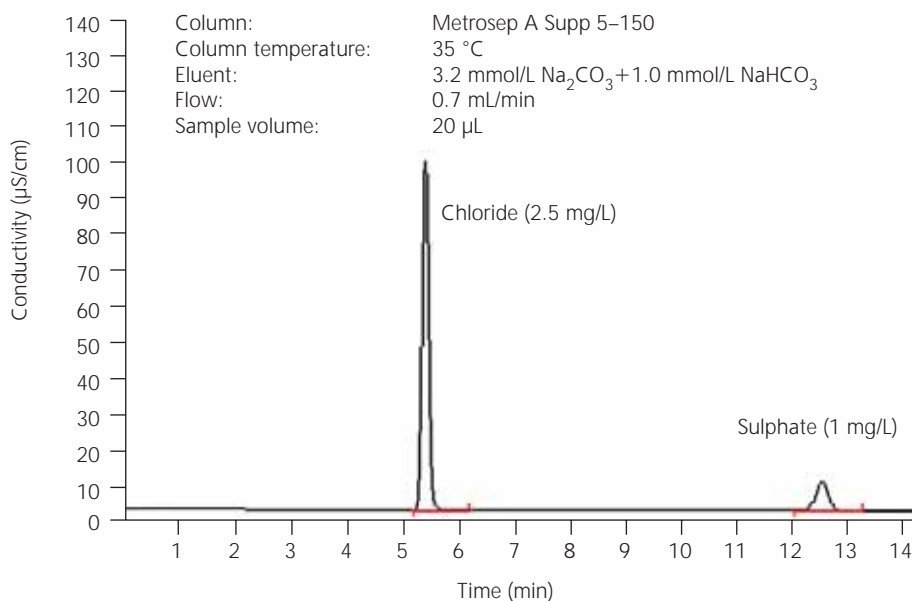


Figure 4: Chromatogram of a denatured ethanol sample spiked with 2.5 mg/L chloride and 1 mg/L sulphate.

ASTM D 7319 stipulates a direct-injection suppressed ion chromatographic method for the determination of both anions. After direct injection, chloride and sulphate are separated on an anion exchange column and then determined quantitatively by suppressed conductivity detection (Figure 4).

Sample preparation

For determining the "potential sulphate", 0.5 mL of a 30% hydrogen peroxide solution is added to 9.5 mL of the ethanol sample. Subsequently, 20 µL are directly injected into the injector of the IC. The analysis can be completely automated by using the 858 Professional Sample Processor.

The limits of detection for chloride and sulphate are 0.6 and 0.2 mg/L, respectively. Even after 1500 ethanol injections containing denaturants and hydrogen peroxide, the analytical unit still provides stable retention times, repeatable peak areas and consistent concentration values.⁴ This highlights the extraordinary ruggedness of the applied micro packed tri-chamber suppressor "MSM II" in long-term use.

The presented direct-injection IC system is 100% solvent compatible and ensures the accurate and precise determination of sulphate, chloride and other anions in full compliance with ASTM D 4806.

Implications

Convenient ion chromatographic methods for the determination of alkali metals, alkaline earth metals, antioxidants as well as chloride and sulphate in biofuels are described. While the antioxidants are detected by UV/vis detection, the metal cations and the anions are determined by non-suppressed and suppressed conductivity detection, respectively. The outstanding performance of ion chromatographic determinations, as illustrated by the recent adoption of ASTM D 7319 in ASTM D 6751 underlines the leading position that IC increasingly assumes in biofuel analysis.

References

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ion analysis

Metrohm AG

Oberdorfstrasse 68, CH-9101, Herisau, Switzerland
 tel. +41 71 353 8585 fax +41 71 353 8901
 Website: www.metrohm.com