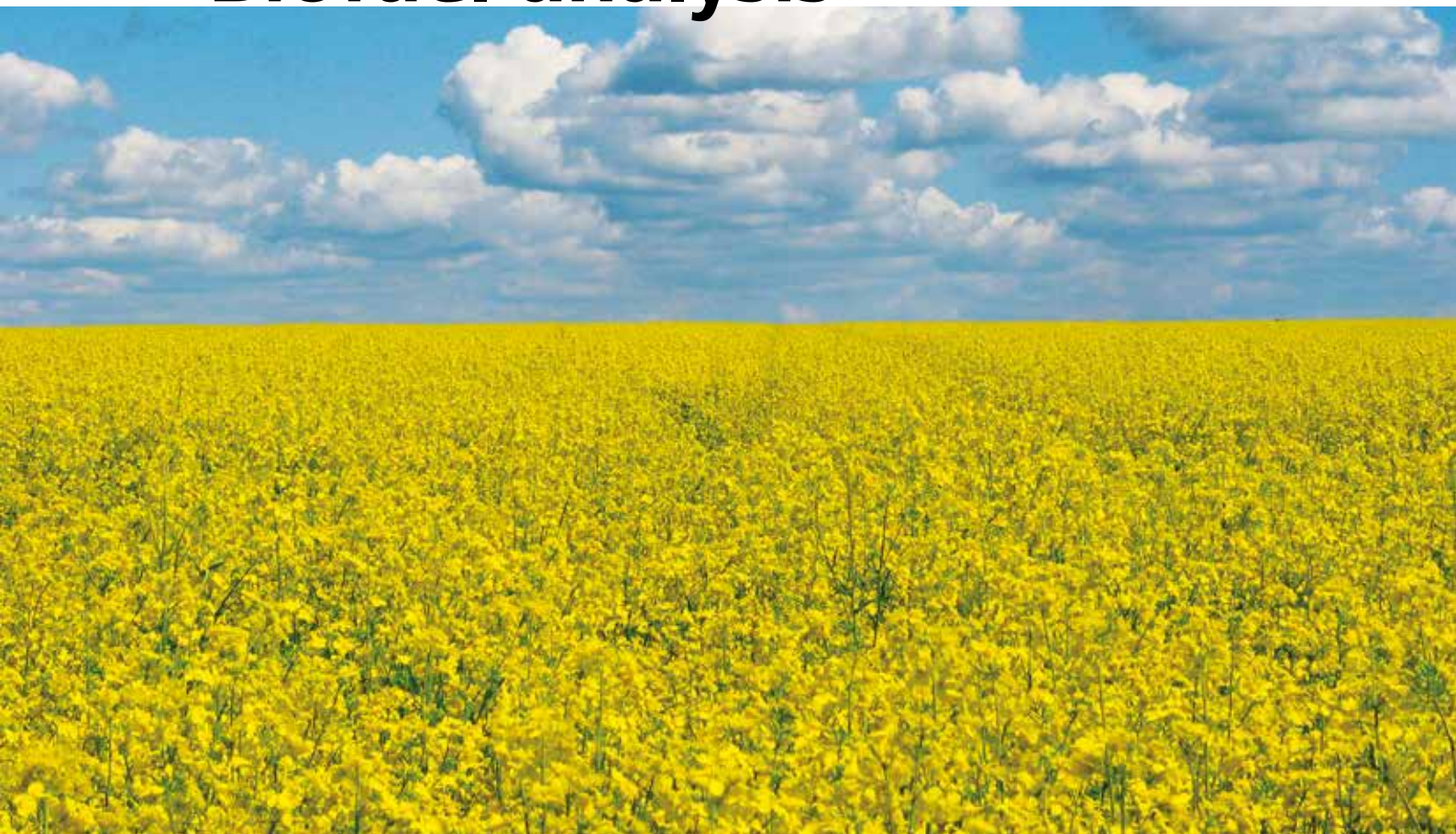


Biofuel analysis



Quality assurance of biofuels



Metrohm ...

- is the global market leader in titration
- offers a complete portfolio for NIR and Raman analysis, in addition to all of the methods of ion analysis – titration, voltammetry, and ion chromatography
- is a Swiss company and manufactures exclusively in Switzerland
- grants a 3-year instrument warranty and a 10-year warranty on chemical suppressors for anion chromatography
- provides you with unparalleled application expertise
- offers you more than 1800 applications free of charge
- supports you with dependable on-site service worldwide
- is not listed on the stock exchange, but is owned by a foundation
- takes a sustainable approach to corporate management, putting the interests of customers and employees ahead of maximizing profit

Metrohm – customized analysis for the biofuel industry

A demanding industry

Sustainable use of biofuels requires reliable and precise analytical methods throughout – from the choice of raw materials through to process optimization and on to the compliant final product.

As a leading manufacturer of instruments for chemical analysis, we are quite aware of these challenges. We offer you state-of-the-art instrumentation helping you to check and improve the quality of biofuels and corresponding blends as well as to comply with the standards – in your laboratory but also atline and online in the process environment.

You can count on our support

Not only do we provide you with the right instrumentation but with complete solutions for the particular task at hand. Your partners at Metrohm are experienced professionals who help you with customized application support and service.

On the following pages, discover the solutions Metrohm offers the biofuel industry in general and you in particular, to ensure the quality and safety of your products.

03



Quality assurance of biofuels

04

Keen interest in biofuels

Interest in biofuels has greatly increased in recent years. The reasons are the diminishing reserves of crude oil and the simultaneous increasing demand for mineral oil as well as the environmental problems linked with burning fossil fuels. In addition to a neutral CO₂ balance, biogenic fuels are generally characterized by their very good microbiological degradability, which is why they are suitable for use in ecologically sensitive areas. Furthermore, alternative fuels can usually be produced locally and thereby reduce dependence on imported raw materials.

Biodiesel and bioethanol production

Biodiesel is usually produced from vegetable oils or animal fats. In an acid-, base-, or enzyme-catalyzed reaction, the triglycerides of the oil or fat are transesterified with methanol to form fatty acid methyl esters (FAME), which are also known generally as biodiesel.

By contrast, bioethanol is made from products that contain sugar or starch. Microbial fermentation of the sugar within the biomass with the help of yeast cultures is a technology that is well-established and widely used commercially. A great hope for the future is cellulosic ethanol made from lignocellulose-containing waste materials, which has so far only been produced in pilot plants. Cellulosic ethanol is characterized by an especially favorable carbon footprint.

High quality standards

Too much water and the presence of alkali metal or alkaline earth metal ions as well as sulfate and chloride ions have a negative effect on the fuel quality and can damage the fuel system of the vehicle. With biofuels based on fatty acids, there is an increased risk of polymerization at higher temperatures in the absence of antioxidants or in the presence of nonferrous metals. With the aim of avoiding these problems, the manufacturers of biofuels and motor vehicles have developed quality standards in which testing methods and quality parameters for biofuels are defined.

A substantial number of the test methods that are stipulated in international standards can be carried out with Metrohm instruments and Metrohm application methods.



Selected standards from the field of biofuel analysis

Minimum requirements and test methods

To ensure the quality of (bio)fuels, there are standards in place that set minimum requirements in the form of limits for impurities and the test methods to be used. Metrohm instruments are highly suitable to carry out the

prescribed test methods listed below to check the limits. If an alternative test method is indicated for monitoring the limits, this is shown by the «√» symbol.

Biodiesel

Biodiesel is sold as a pure fuel and in blends with fossil fuels. The minimum requirements are set out in the specifications EN 14214 (pure fuel and blend stock) and ASTM D6751 (only blend stock). EN 14213 describes the

minimum requirements for biodiesel used as heating oil. EN 590 applies to diesel fuels that contain up to 7% biodiesel and ASTM D7467 applies to those that contain between 6 and 20% biodiesel.

Test method	Requirements and test methods			Method	Page	
	EN 14214 EN 14213	ASTM D4806 ASTM D7467	EN 590			
Acid number	EN 14104	ASTM D664	–	Titration	7	
Iodine number	EN 14111	–	–	Titration		
Water content	EN ISO 12937	√	EN ISO 12937	KFT _{coulometric}	10	
Oxidation stability	EN 15751 (EN 14112)	EN 15751 (EN 14112)	EN 15751 ^a	EN 16568 ^b	Oxidation stability	12
Free and total glycerol	√	ASTM D7591	–	Ion chromatography	14	
Alkali metal and alkaline earth metal	√	√	–	Ion chromatography	15	
Antioxidants	recommended	recommended	recommended	Ion chromatography		
Sulfur content	√	√	√	CIC	18	

KFT = Karl Fischer Titration, CIC = Combustion Ion Chromatography

^aApplies to pure biodiesel and blends that contain at least 2% (v/v) biodiesel

^bAging of the sample proceeds at 120 °C instead of 110 °C as stipulated in EN 15751

Bioethanol

The minimum requirements for bioethanol as a blend component in gasoline are documented in standards EN 15376

and ASTM D4806. ASTM D5798 relates to ethanol-gasoline blends E75–E85.

Test method	Requirements and test methods		Method	Page
	EN 15376 4545	ASTM D4806 ASTM D5798		
pH _e value	EN 15490	ASTM D6423	pH _e value	6
Conductivity	DIN 51627-4	–	Conductivity	
Total acid number and acidity	EN 15491	ASTM D1613	Titration	8
Inorganic chloride content	EN 15484	ASTM D512	Titration	
Total inorganic sulfate content	–	ASTM D7318	Titration	
Water content	EN 15489	ASTM E1064	KFT _{coulometric}	11
	–	ASTM E203	KFT _{volumetric}	
Inorganic chloride content	EN 15492	ASTM D7319	Ion chromatography	16
		ASTM D7328		
Total and potential inorganic sulfate content	EN 15492	ASTM D7319	Ion chromatography	16
		ASTM D7328		
Sulfur content	√	√	CIC	18
Copper content	√	√	Voltammetry	20

KFT = Karl Fischer Titration, CIC = Combustion Ion Chromatography

Further test methods for the fuel sector that comply with the standards can be found in the brochure «Petrochemical analysis» (8.000.5143EN).

pH_e value and conductivity measurement

06

Bioethanol

pH_e value

A combined pH glass electrode with ground-joint diaphragm is recommended for measuring the pH value in organic solvents. Because pH_e determination according to ASTM D6423 and EN 15490 is time-controlled, it is essential that the sensor has a rapid response time. The EtOH-Trode with a special membrane glass and the very precise fixed ground-joint diaphragm is particularly suitable for measuring the pH_e values of biofuels. The double-junction system allows the free choice of the electrolyte (e.g., 3 mol/L KCl in ASTM D6423 and 1 mol/L LiCl in EN 15490). The pH meter used for the measurement should possess the following GLP functions, among others:

- Three-point calibration with automatic buffer recognition
- Temperature compensation
- Calibration data monitoring
- Automatic measured value recording
- Result memory with identification

The pH meter 827 pH lab for laboratory use and the handy, battery-operated 826 pH mobile offer all these functions with extremely comfortable operation.

Conductivity

Electrical conductivity is an important analytical sum parameter for detecting and monitoring corrosive ionic constituents in ethanol and ethanol fuel. Because of the considerably lower conductivity in nonaqueous systems, very sensitive measuring systems are required. The stainless-steel conductivity measuring cell (6.0916.040) with Pt 1000 temperature sensor, in conjunction with the flexible 856 Conductivity Module, is ideally suited for this application in accordance with DIN 51627-4.



The electrode for measuring pH_e values in ethanol



The laboratory pH meter 827 pH lab



Titration

Biodiesel

Acid number

The acid number is a sum parameter for all acidic components; at the same time it is a measure for the long-term stability and corrosiveness of the biofuel. The smaller the value, the higher the quality. Standard EN 14104 stipulates a nonaqueous potentiometric acid-base titration for determining the acid number. This involves dissolving the sample in a bioethanol-diethyl ether mixture and titrating it with potassium hydroxide dissolved in 2-propanol (0.1 mol/L).

As organic solvents are used, the manual working steps should be reduced to a minimum. With its space-saving Dosino technology, the Titrando allows fully automatic and safe solvent addition. The Solvotrode, an excellently shielded combined pH glass electrode, has been specially developed for nonaqueous titrations. The separable ground-joint diaphragm guarantees stable potentials and is easy to clean. Extremely comfortable, rapid and precise is the determination when using the automated analysis system MATi 02.

Iodine number

The iodine number is a measure for the number of double bonds in a sample. It is the amount of iodine (in g/100 g sample) that can be added to the sample under the given conditions. The determination of the iodine number in fatty acids or biodiesel is covered by European standard EN 14111.

An aliquot of the fatty acid or biodiesel sample is dissolved in a mixture of cyclohexane and glacial acetic acid and treated with Wijs reagent. After a defined time has elapsed, potassium iodide and water are added. The released elemental iodine is then titrated with sodium thiosulfate solution. EN 14111 allows both optical (with starch solution as the indicator) and potentiometric end-point determination.



Bioethanol

Chloride content

The chloride content in bioethanol fuels is the subject of ASTM D512. Quantitation can be carried out by mercurimetric or argentometric titration or by direct determination with a Cl-selective electrode. Argentometric titration (with silver nitrate) is the method of choice because of its environmental advantages and very high precision. A defined volume of the sample is pipetted into the titration cell, treated with 5 mL nitric acid (2 mol/L), and then titrated against silver nitrate solution (0.01 mol/L). Accordingly, EN 15484 in EN 15376 describes the potentiometric titration of inorganic chlorides with a 0.1 mol/L solution of silver nitrate after dissolving the evaporation residue in deionized water.

Acidity and total acid number

Standards ASTM D4806, ASTM D5798, and EN 15376 set out the maximum permissible acid content in bioethanol. The two test methods stipulated therein (ASTM D1613, EN 15491) specify acid-base titration with visual indicator endpoint detection.

Sulfate content

A proven method for sulfate determination according to ASTM D7318 is potentiometric titration with lead nitrate using a Pb-selective electrode. The pH value of the sample is adjusted to pH 3–5 with perchloric acid and the sulfate is then precipitated out with lead nitrate solution. The Pb-selective electrode detects the first excess of lead ions at the equivalence point.



The Titrando – the allrounder for potentiometric titration

The wide range of potentiometric applications for bio-fuels requires a highly flexible titrator. No other titration system offers more flexibility and ease of use than the Titrando.

- With Touch Control or **tiamo** – titration and more – operation is perfectly easy.
- The space-saving Dosino technology with numerous liquid handling functions simplifies sample preparation and allows automatic preparation and emptying of burets without operator intervention – it is no longer necessary to handle organic solvents.
- Intelligent dosing units and electrodes eliminate confusion. Extensive GLP functions guarantee safe and error-free work.
- The Titrando is unbelievably flexible – it covers the whole range from a simple stand-alone titrator up to a fully automatic titration system with sample changer, direct balance connection and barcode reader.

09



The Titrando offers maximum flexibility and operating comfort.

Water determination according to Karl Fischer

10

The presence of water in biofuels reduces their calorific value and increases the corrosion rate.

Biodiesel

Water as a contaminant

Water hydrolyzes the ester bonds of fatty acid methyl esters, leading to the formation of fatty acids. Consuming additional NaOH, these acids form soaps, which make the subsequent removal of glycerol more difficult. Biodiesel with a high water content has a clearly lower oxidation stability. The lower the latter, the greater the probability that oxidation products will be formed during a longer storage period. These could damage the engine, in particular the fuel injection system, by forming deposits.

Maximum permissible water content

To avoid the drawbacks mentioned above, EN 14214 limits the water content of biodiesel to 500 mg/kg. Test method EN ISO 12937 «Petroleum products – Determination of water – Coulometric Karl Fischer titration method» specified in EN 14214 describes the coulometric Karl Fischer titration for determining the water content.

Coulometer and Titrand

All coulometers from Metrohm easily meet all the specifications stipulated in the standard and are outstandingly suitable for this application. In most cases, the sample can be injected directly into the reaction solution. To improve the solubility of the samples, xylene (dimethylbenzene) is added to the KF reagent.

Karl Fischer oven method

Some biodiesel fuels contain additives that could participate in side reactions during the direct coulometric Karl Fischer titration. In such cases, Metrohm recommends that the biodiesel sample is not injected directly into the reaction solution. Instead, the water contained in the biodiesel should be driven off in a Karl Fischer oven. The 860 KF Thermoprep is suitable for this. The water is driven off at 120 °C and transported to the titration cell of the KF Coulometer in a stream of carrier gas (dry air or inert gas). This process can be completely automated with the 874 USB Oven Sample Processor.



874 USB Oven Sample Processor with 851 Titrand for the automatic determination of the water content in samples containing oil. Side reactions and contamination of the KF coulometer cell are avoided.



852 Titrand with coulometric and volumetric titration cell for determining trace amounts of water



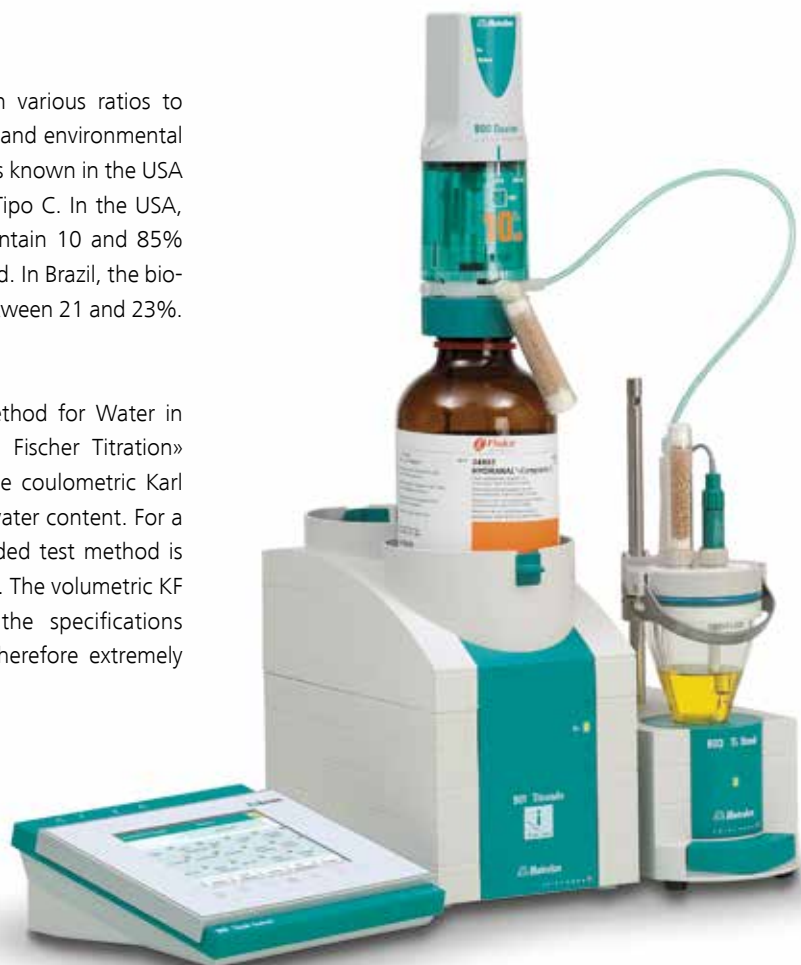
Bioethanol

Gasoline-alcohol blends

Bioethanol is mixed with gasoline in various ratios to reduce both the demand for gasoline and environmental pollution. The gasoline-alcohol blend is known in the USA as gasohol and in Brazil as Gasolina Tipo C. In the USA, the mixtures E10 and E85, which contain 10 and 85% bioethanol respectively, are widespread. In Brazil, the bioethanol content of most blends lies between 21 and 23%.

Test methods

The ASTM E1064 «Standard Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration» and EN 15489 standards describe the coulometric Karl Fischer titration for determining the water content. For a water content > 2%, the recommended test method is volumetric titration as per ASTM E203. The volumetric KF titrators from Metrohm meet all the specifications required by the standards and are therefore extremely suitable for this application.



901 Titrando with 900 Touch Control and 803 Ti Stand

Oxidation stability

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Biodiesel

Fatty acid methyl esters are produced from a vegetable oil, usually obtained from oil seed, by transesterification with methanol. Both feedstock and biodiesel have a relatively short storage life as they are slowly oxidized by atmospheric oxygen. The resulting oxidation products can damage vehicle engines. For this reason, the oxidation stability is an important quality criterion for biodiesel and vegetable oils and must therefore be checked regularly during manufacture and storage.

International quality standards

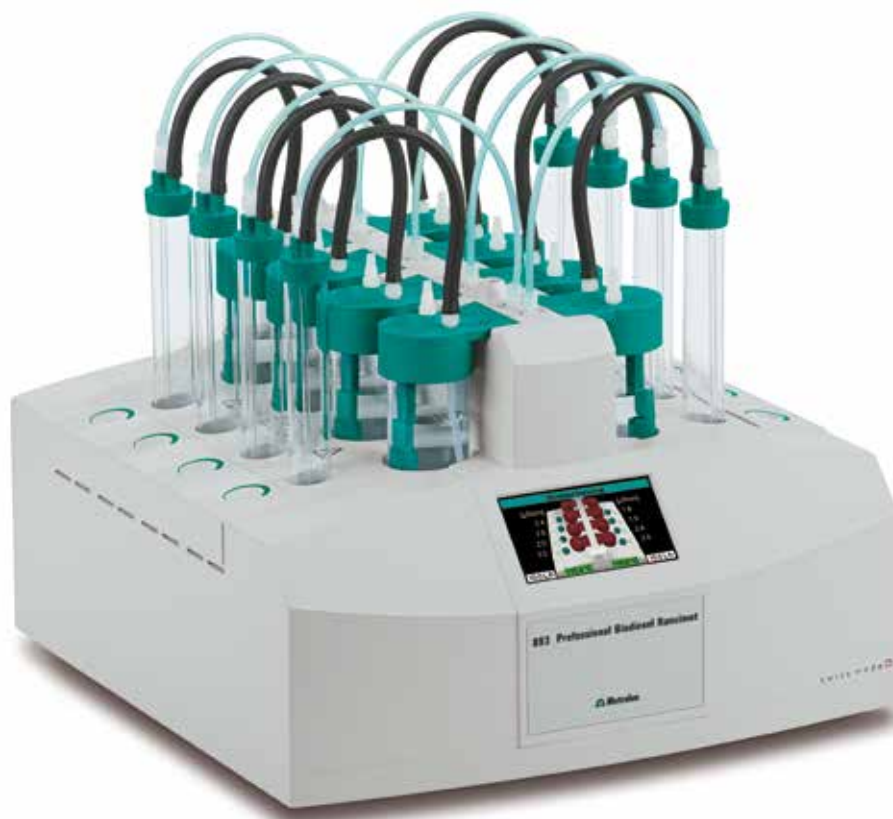
The oxidation stability of fatty acid methyl esters is included as an essential parameter in many standards, as indicated in the table on page 5. They define the minimum quality requirements of biodiesel that is sold as a fuel or heating oil.

Measuring principle

To determine the oxidation stability with the Rancimat method, air is passed through the sample at an elevated temperature to cause artificial aging. During this process long-chain organic molecules are oxidized by oxygen, whereby highly volatile organic substances form besides insoluble polymer compounds. The former are driven out by a stream of air, absorbed in water, and detected there by measuring the conductivity. The time until these decomposition products form is referred to as the induction time or the Oil Stability Index (OSI) and characterizes the resistance of the sample to oxidative aging processes, that is, the oxidation stability.

893 Professional Biodiesel Rancimat and StabNet software

The 893 Professional Biodiesel Rancimat is a modern, PC-controlled instrument that allows the simple and reliable determination of oxidation stability in biodiesel and biodiesel blends. Up to eight samples can be measured simultaneously. The effectiveness of antioxidants can also be determined with the 893 Professional Biodiesel Rancimat.



The 893 Professional Biodiesel Rancimat allows oxidation stability to be determined in accordance with numerous international standards.



Start buttons on the instrument

Next to each measuring position there is a button with which determination can be started immediately after the sample has been placed in the heating block. The start button is completely sealed on the outside, so no liquids such as sample or water can enter.



Cover with built-in conductivity cell

The conductivity cell, with its electrical connections, is incorporated in the measuring vessel cover. When the cover is placed in position, the cell is immersed in the water and is immediately in the right position. At the same time electrical contact is made to the measuring electronics in the instrument.



Modern Software for stability measurements

StabNet is the modern and user-friendly software for carrying out stability measurements and archiving the measurement data. The characteristic features of StabNet are its ease of use and flexibility.

Further advantages of StabNet

- Database with flexible filtering, sorting and statistical functions
- Network-compatible due to client-server functionality
- Meets all the requirements of FDA and GLP

Ion chromatography

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State-of-the-art ion chromatography (IC) permits the efficient separation and determination of inorganic and low-molecular weight organic anions and cations. Different separation mechanisms and detection types as well as the possibility of automation and sample preparation render IC a versatile analytical technique for the biofuel and petrochemical industry.

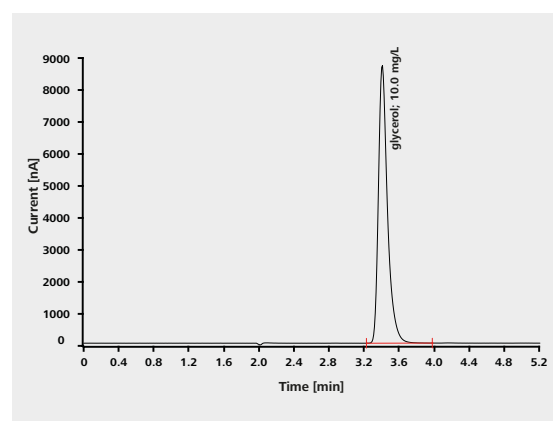
Biodiesel

Glycerol

The production of biodiesel from vegetable oils and animal fats leads to the formation of free and bound glycerol

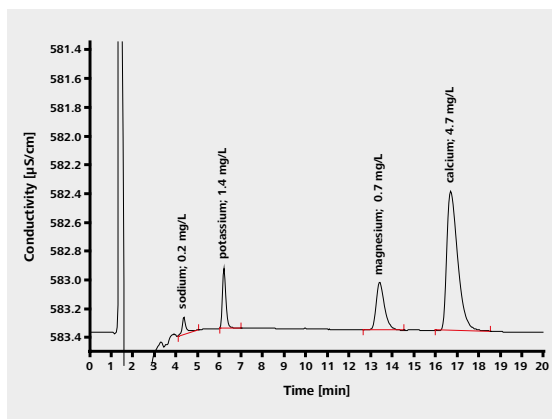
(monoglycerides and diglycerides) as by-products after transesterification of the triglycerides. Incomplete transesterification and/or separation of glycerol causes glycerol contamination in the biodiesel, which speeds up fuel aging and leads to deposits in the engine and blocked filters. To ensure engines operate properly, the American ASTM D6751 and the European EN 14214 limit the maximum total glycerol content (i.e., free and bound glycerol) to 0.24 and 0.25% (v/v), respectively. Free and bound glycerol is determined by ion chromatography and subsequent pulsed amperometric detection in accordance with ASTM D7591.

Glycerol determination using pulsed amperometric detection; column: Metrosep Carb 2 - 150/4.0; eluent: 100 mmol/L NaOH, 10 mmol/L sodium acetate, 1 mL/min; column temperature: 30 °C, sample volume: 20 µL



Alkali metals and alkaline earth metals

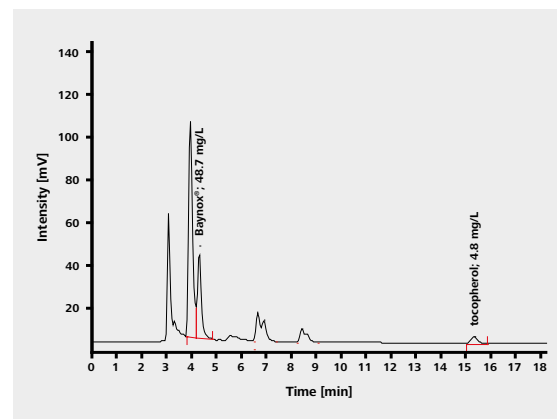
Whereas sodium and potassium contaminants stem from the hydroxides used in transesterification, calcium and magnesium impurities result mainly from the use of the water employed in biodiesel washing to extract water-soluble foreign substances such as methanol and glycerol. In higher concentrations, these metals cause operating problems in the engine, which is why their concentration in the fuel is regulated by international specifications. Both EN 14214 and ASTM D6751 allow a maximum total concentration of 5 mg/kg for the two alkali metals and the two alkaline earth metals, respectively.



Alkali and alkaline earth metals in a biodiesel sample. The samples are extracted with dilute nitric acid, dialyzed, and then injected directly into the IC system. The complete sample preparation procedure and analysis takes place fully automatically. Column: Metrosep C 4 - 150/4.0; eluent: 2 mmol/L HNO₃ with 10% acetone, 0.9 mL/min; column temperature: 30 °C; sample volume: 10 µL

Antioxidants

The oxidation stability of fatty acids and of the fatty acid methyl esters synthesized from them can be significantly improved by adding antioxidants. Biodiesel based on rapeseed oil already contains a natural protection against oxidation – vitamin E (d- α -tocopherol). In addition, one of the Baynox[®] products, whose structures were inspired by that of vitamin E, is added to the biodiesel as a stabilizer. Both antioxidants inhibit both oxidation to corrosive acids and formation of insoluble polymers and thus prevent the injection nozzles from being blocked. Antioxidants are determined in the course of quality control, especially for monitoring and assessing storage stability. The chromophores present in vitamin E and Baynox[®] allow sensitive spectrophotometric detection without prior post-column derivatization.



Biodiesel fuel spiked with 50 mg/L Baynox[®] and 5 mg/L α -tocopherol. To improve solubility, dichloromethane is added to the eluent and analyte solutions. Column: Prontosil 120-5-C18; eluent: 90% acetonitrile and 10% dichloromethane, 1.0 mL/min; column temperature: 35 °C; wavelength: 220 nm; sample volume: 10 µL; sample dilution 1:1000 (w/w)



940 Professional IC Vario for fully automatic cation determination with Metrohm Inline Extraction and Inline Dialysis



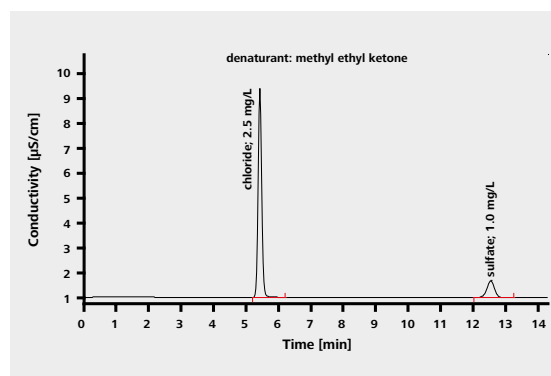
Bioethanol

Chloride and sulfate

Bioethanol is either used in pure form as a fuel or blended with fossil fuels. Contaminants in the form of inorganic chloride and sulfate salts are corrosive and lead to deposits and blockages in the fuel filter and injection nozzles. The international ethanol specifications EN 15376, ASTM D4806, and ASTM D5798 regulate the sulfate and chloride content in bioethanol and in bioethanol fuel blends.

According to ASTM D7319, the total content of inorganic chloride and sulfate is determined after direct injection of the ethanol sample and separation on an anion-exchange column by conductivity detection. If hydrogen peroxide is previously added, sulfur-containing species such as sulfites, sulfides, or thiosulfates can be oxidized to form sulfate and are quantified as potential sulfate content. The analytical system is extremely robust and guarantees outstanding reproducibility and repeatability even after 1500 determinations carried out in round robin tests.

In addition, there are also the ion chromatographic methods described in ASTM D7328 and EN 15492: before injection, the denatured ethanol sample is evaporated to dryness and then diluted for injection with 1% solution of hydrogen peroxide (ASTM D7328) or with deionized water (EN 15492).



Chromatogram of a denatured ethanol sample spiked with 2.5 mg/L chloride and 1 mg/L sulfate; column: Metrosep A Supp 5 - 150/4.0; eluent: 3.2 mmol/L Na_2CO_3 , 1 mmol/L NaHCO_3 , 0.7 mL/min; column temperature: 35 °C; sample volume: 10 μL

Cellulosic ethanol

Carbohydrates and organic acids

Cellulosic ethanol is one of the second-generation biofuels and is produced in pilot plants from lignocellulose-containing waste materials such as straw, wood, and bagasse. Compared with bioethanol made from starch and sugar cane, it has a considerably better carbon footprint. Furthermore, the cheap raw materials needed to produce it are not in competition with food production. The biomass, however, which is made up of complex sugars, needs to undergo chemical or thermal pretreat-

ment before fermentation and then has to be converted into fermentable sugars using special enzymes. Frequently, during pretreatment of the plant material, fermentation inhibitors appear in the form of carbohydrates and organic acids (e.g., gluconic acid), which kill the microorganisms used in the subsequent fermentation. Fast and sensitive ion chromatographic determination of organic acids and carbohydrates contributes substantially to the optimization of the fermentation process.

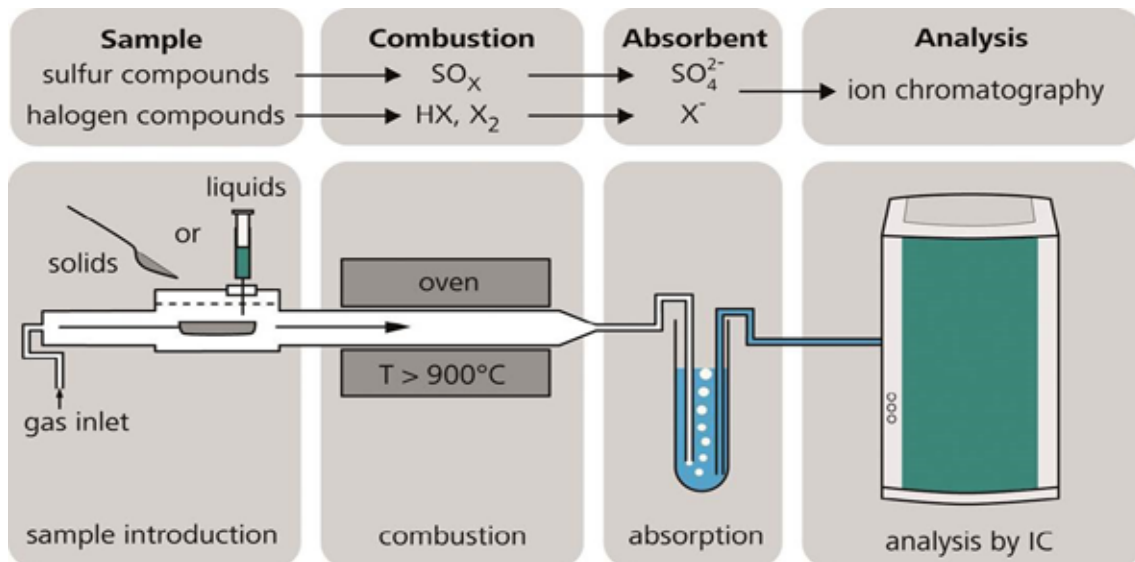


Fuel blends

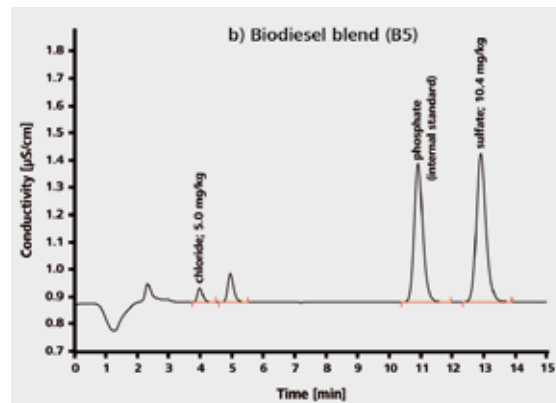
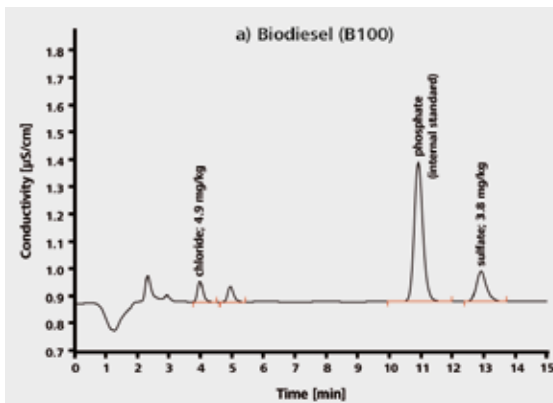
Sulfur content

The burning of sulfur-containing fuels leads to the emission of air-polluting sulfur oxides into the atmosphere. Furthermore, high sulfur concentrations have an adverse effect on the ease of ignition of fuels and their stability during storage. A fast and reliable method for determining the sulfur content is required. Combustion IC allows

the determination of the sulfur and halogen content in combustible solid and liquid matrices by combining combustion digestion (pyrolysis) with subsequent ion chromatography. It can be fully automated and excels in its high sample throughput and excellent precision and accuracy.



In combustion digestion (pyrolysis), sulfur compounds are converted into sulfur dioxide, and halogen compounds are converted into hydrogen halides and elemental halogens. These gaseous combustion products are fed into an oxidizing absorption solution and detected as sulfate and halide by way of the ion chromatography that follows.



Determination of the sulfur and chlorine content in a) B100 biodiesel sample and b) B5 biodiesel blend; column: Metrosep A Supp 5 - 150/4.0; eluent: 3.2 mmol/L Na_2CO_3 , 1.0 mmol/L NaHCO_3 , 0.7 mL/min; column temperature: 30 °C; sample volume: 100 μL , absorption solution: 30 mg/L H_2O_2

Voltammetry

20

Voltammetric trace analysis is used for determining electrochemically active substances. These can be inorganic or organic ions or even neutral organic compounds. Voltammetry is often used for supplementing and validating spectroscopic methods and is characterized by low equipment costs, comparably low investment and operating costs, short analysis times, and an outstanding accuracy and sensitivity. Unlike spectroscopic methods, voltammetry can also differentiate between different oxidation states of metal ions or between free and bound metal ions. This is referred to as speciation analysis.

Broad application range

Voltammetric measurements can be carried out both in aqueous solutions and in organic solvents. Heavy metal

determinations are usually carried out in aqueous solutions after digestion of the sample.

Voltammetry is suitable in particular for laboratories in which, with a medium sample throughput, only a few parameters need to be controlled. It is often used for specific applications that are either not feasible or too costly using other techniques.

884 Professional VA

The 884 Professional VA is a flexible measuring instrument for accurate and sensitive voltammetric and polarographic analyses. The analyses can be easily automated by adding Dosinos and a sample changer. The accompanying viva software enables individual optimization of methods.

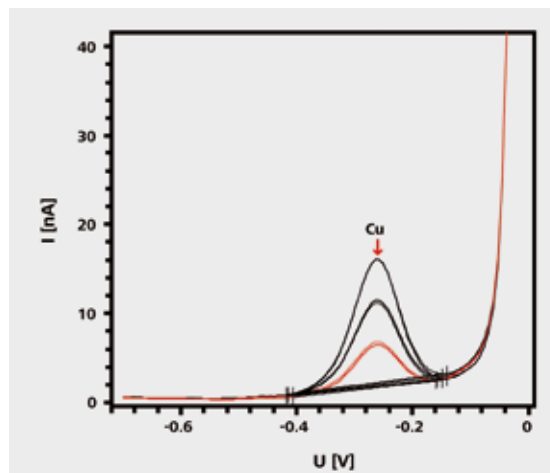




Bioethanol

Copper

Ethanol is used increasingly in gasoline as a blending component. Contaminants can cause problems in the engine. For example, traces of copper catalyze the oxidation of hydrocarbons. As a consequence, polymer compounds can form that can lead to deposits and blockages in the fuel system. Specifications EN 15376 and ASTM D4806 describe the minimum requirements for ethanol that is blended with gasoline and allow a copper content of 100 $\mu\text{g}/\text{kg}$. By contrast, standard ASTM D5798 sets the copper content in ethanol-gasoline blends E75-E85 at 70 $\mu\text{g}/\text{L}$. Using voltammetry, copper can be measured without any sample preparation in pure ethanol or ethanol-gasoline blends (E85, 85% ethanol and 15% gasoline) in the range between 2 and 500 $\mu\text{g}/\text{kg}$.



Voltammetric determination of copper

Potentiostats and galvanostats

22

Corrosion resistance in biofuels and biofuel blends

The corrosion resistance of storage tanks, process pipe-work, and pipelines is an important material requirement for the storage and transportation of fuels. The materials along which fuels are conveyed, especially, can suffer considerable damage due to stress corrosion cracking (SCC) and microbially-induced corrosion (MIC). Whereas the corrosion behavior occurring in relation to fossil fuels has been adequately studied and documented – like, for example, in ASTM D7548 – systematic studies of biofuel corrosion are still lacking to a large extent. What is clear, is that, owing to the various chemical and physical properties, fossil fuels and biofuels differently influence the corrosion behavior at the interface between the material and fuel. Corrosion behavior is generally expressed in terms of the corrosion potential as a characteristic electrochemical value.

Biodiesel shows a high corrosion potential

Biodiesel has a higher electrical conductivity and is more hygroscopic than conventional diesel fuel. This means that, when stored for a long time, it absorbs more water, which in turn leads to hydrolysis of the ester bonds and thus to the formation of free fatty acids. The pH value falls and the microbiological activity responsible for degradation increases. With the biotic degradation reactions, the properties of the biodiesel also change; in particular, the corrosion potential at the material-fuel interface increases.





The material-fuel interface

Electrochemical methods provide the possibility for determining the corrosion resistance of various materials in fuels easily and conveniently. The Autolab PGSTAT100N potentiostat/galvanostat combined with the FRA2 Impedance Analyzer Module is a powerful analytical system

that incorporates a large number of preprogrammed methods. For example, the corrosion processes taking place on the conducting material-fuel interface can be determined effectively by linear polarization or electrochemical impedance spectroscopy (EIS).



The Autolab PGSTAT100N – a potentiostat/galvanostat for electrochemical determinations (maximum 100 V compliance voltage) in media with low conductivity

Process analysis

24

Customized process control

In the biofuel industry, continuous control of the production process as well as the monitoring of the product quality and the composition of any waste streams is crucial. With the process analyzers of Metrohm Process Analytics, this is possible 24 hours a day, 7 days a week. The analyzers are used directly on-site, as close as possible to the process, and run completely stand-alone without operator intervention. Moreover, it does not make a difference whether a single parameter is to be determined in a single sample stream or several different parameters are to be determined in complex, multiple sample streams – the Metrohm Process Analytics engineers provide you with the appropriate online or atline analyzer.

Proven wet-chemistry methods

The Applikon analyzers are based on wet-chemical analysis techniques such as titration, colorimetry, or ion-selective electrode measurements. In online analysis, sampling and sample preconditioning are at least as important as the analyzer itself. Metrohm Process Analytics has a lot of expertise in this area and is capable of offering customized sampling systems, for example, for pressure reduction, filtering, and degassing.

Network integration

The online analyzers from Metrohm Process Analytics are all equipped with possibilities for digital as well as analog outputs. Results, for example, can be transferred via 4–20 mA outputs, whereas alarms can be transmitted via digital outputs. Digital inputs, in turn, can be used for remote start-stop purposes.

Robust design

In many cases, the IP66-NEMA4 housing of the analyzers will be sufficient. In some cases in the biofuel industry, however, explosion-proof systems are required. For those circumstances, the ADI 2045Ti Ex proof Analyzer is available in a stainless-steel explosion-proof version for Zone I or Zone II according to the explosive atmosphere directives (ATEX).

 **Metrohm**
Process Analytics



Many of the analysis methods that are used in the laboratory can be transferred to an online analyzer. Typical applications are:

Water content

Presence of too much water in the fuel reduces the calorific value, promotes corrosion, encourages bacterial growth, and increases the likelihood that oxidation products will form. As in the laboratory, Karl Fischer titration, particularly coulometry, is the method of choice for the online determination of the water content in any biofuels. Analyzers from Metrohm Process Analytics allow determination in either one or more than one sample streams.



ADI 2045Ti Process Analyzer for coulometric determination of water content according to Karl Fischer

Potassium

Potassium residues in biodiesel result from the catalyst and lead to deposits in the fuel injection system. They are determined with ion-selective electrodes. Depending on the required limit of detection, the determination can be carried out either with an ALERT analyzer or with the ADI 2018 analyzer, which is equipped with high-precision piston burets and is therefore more precise.

Free fatty acids (FFA)

An excessively high proportion of free fatty acids promotes corrosion and, together with the catalyst, leads to soap formation. In addition, a rising concentration of free fatty acids in the biodiesel is usually a sign of the



Cuvette for colorimetric determinations

hydrolysis of the fatty acid methyl esters that is initiated by the penetration of water. FFA determination is also used in initial checking of the vegetable oils used in transesterification. Determination is carried out in the ADI 2045Ti analyzer using colorimetric titration or, if there is severe turbidity, potentiometric titration.

Total phosphate content

Phosphate contamination in biodiesel results from the phospholipids that occur ubiquitously in vegetable oils and from the phosphoric acid added during the production process. After UV digestion in the presence of sulfuric acid, the resulting orthophosphate is determined colorimetrically. The combination of digestion and colorimetric determination is only possible in the ADI 2045Ti Process Analyzer.



ADI 2045Ti analyzer for determining the total phosphate content



Metrohm Quality Service – service you can rely on

Reliable results – for the lifetime of the analyzer

Chemical analysis accompanies the biofuel industry from the choice of raw materials, through specification-compliant production, and on to end product quality control. Whoever is responsible in the laboratory for the accuracy of the results must not make compromises. The golden rule here is that professionally installed and commissioned systems that are serviced regularly guarantee the greatest possible reliability.

With Metrohm Quality Service you are on the safe side from day one. From installation and start-up, to regular maintenance and fast repair – if problems arise – we guarantee that you can rely on your instrument and gain maximum uptime from your investment.

Metrohm Compliance Service

You can trust Metrohm Compliance Service when it comes to the professional qualification of your analyzers. Installation Qualification/Operational Qualification (IQ/OQ) or Certified Installation (CI) saves you time and money because we configure the system according to your requirements and ensure quick and reliable commissioning.

User instructions lay the foundations for safe, error-free operation. The Metrohm Compliance Service also includes comprehensive documentation and guarantees compliance with the standards of quality management systems such as GLP/GMP and ISO.



Metrohm Quality Service

Metrohm's global Quality Service, and regularly scheduled preventive maintenance in particular, extends your instrument's lifetime and ensures trouble-free operation. Maintenance work is carried out by qualified and certified service engineers. You have the option of selecting different types of service contracts depending on your

particular need. With a Total Care Contract, for example, you can rely on the optimum performance of your Metrohm instruments at all times, incurring no additional costs whatsoever and benefit from complete and compliant documentation.

Metrohm Quality Service	Customer benefits
Metrohm Care Contracts	<ul style="list-style-type: none"> • Minimizes downtime through preventative maintenance • Cost control and savings through free or discounted replacement materials and consumables • Guaranteed reaction times and rapid on-site repair • Documented instrument certification as an ideal preparation for audits
Metrohm Software Care	<ul style="list-style-type: none"> • High data security and maximum system performance through regular, professional software maintenance
Metrohm Compliance Service	<ul style="list-style-type: none"> • Customized services and documentation for analytical instrument qualification (AIQ) • Professional start-up (IQ/OQ or Certified Installation) and requalification or recertification by specifically trained employees
Metrohm Remote Support	<ul style="list-style-type: none"> • Quick resolution of software and application issues directly at the workplace
Metrohm Dosing Test	<ul style="list-style-type: none"> • Calibration of burettes (e.g., dosing and exchange units) with certification • Accurate measurement results • Verification documentation for compliance with regulations and efficient audits
Metrohm Repair Service	<ul style="list-style-type: none"> • Rapid availability of repaired instruments thanks to decentralized repair workshops around the world and a central workshop at the manufacturer site • Highly qualified service technicians ensure sustainable repair success • Rapid resolution of problems and minimized downtimes through on-site emergency services and express repairs
Metrohm Spare Parts	<ul style="list-style-type: none"> • Original spare parts, made in Switzerland and available worldwide • Short delivery times through warehousing from local distributors • Investment security through ten-year spare parts guarantee after discontinuation
Metrohm Application Support	<ul style="list-style-type: none"> • Free access to the Metrohm Application Finder (www.metrohm.com/en/applications/) with more than 1800 applications (Application Bulletins, Application Notes, monographs, technical posters, and technical articles) • Rapid and professional resolution of any application issues through personal consultations with our specialists by e-mail, telephone, or remote support • Support for the solution of complex analytical problems, as well as method optimization on-site or at our application laboratories
Metrohm Training Programs	<ul style="list-style-type: none"> • Basic and advanced training with local representatives, at the Metrohm Academy or directly on-site • Efficient and proper use of all analytical methods, as well as results reliability through competently trained users • Training documentation and certificates for trouble-free audits

Ordering information

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pH_e and conductivity measurement

pH_e measurement in bioethanol

2.827.0X1X	827 pH lab with Pimatrode or Unitrode
2.826.0010	826 pH mobile
6.0269.100	EtOH-Trode
6.2104.020	Electrode cable

Conductivity measurement in bioethanol

2.856.0110	856 Conductivity Module with 900 Touch Control
6.0916.040	Conductivity measuring cell (stainless steel) $c = 0.1 \text{ cm}^{-1}$ with Pt 1000
6.1418.250	Titration cell with thermostat jacket
6.1414.010	Titration cell lid with 5 openings

Titration

Acid number in biodiesel

2.905.0010	905 Titrande
2.900.0010	900 Touch Control
2.801.0040	801 Magnetic Stirrer
2.800.0010	800 Dosino (2 × for addition of titrant and solvent)
2.814.0030	814 USB Sample Processor
MATi 02	Automated TAN/TBN determination
6.3032.220	Dosing Unit 20 mL (titrant)
6.3032.250	Dosing Unit 50 mL (solvent)
6.0229.010	Solvotrode <i>easyClean</i> , fixed cable, plug F
6.2320.000	Electrolyte TEABr = 0.4 mol/L in ethylene glycol

Iodine number in biodiesel

2.905.0010	905 Titrande
2.900.0010	900 Touch Control
2.801.0040	801 Magnetic Stirrer
2.800.0010	800 Dosino
6.3032.220	Dosing Unit 20 mL (titrant)
6.0471.300	iPt-Titrode

Chloride in bioethanol

2.905.0010	905 Titrande
2.900.0010	900 Touch Control
2.801.0040	801 Magnetic Stirrer
2.800.0010	800 Dosino (2 × for addition of titrant and nitric acid)
6.3032.220	Dosing Unit 20 mL (titrant)
6.3032.210	Dosing Unit 10 mL (nitric acid)
6.0470.300	iAg-Titrode

Sulfate in bioethanol

2.905.0010	905 Titrande
2.900.0010	900 Touch Control
2.801.0040	801 Magnetic Stirrer
2.800.0010	Dosino (2 × for addition of titrant and perchloric acid)



6.3032.220	Dosing Unit 20 mL (titrant)
6.3032.210	Dosing Unit 10 mL (perchloric acid)
6.0502.170	Pb-selective electrode
6.0750.100	LL ISE Reference
6.2104.020	Electrode cable, 1 m, F
6.2106.020	Cable strand, 1 m, 2 × B

Water determination according to Karl Fischer

Coulometric KF Titration

2.831.0010	831 KF Coulometer including generator electrode with diaphragm and Stirrer
2.756.0010	756 KF Coulometer including generator electrode with diaphragm, 728 Stirrer and integrated printer
2.851.0010	851 Titrand including generator electrode with diaphragm and 801 Magnetic Stirrer
2.899.0010	899 Coulometer including generator electrode with diaphragm and stirrer

Volumetric KF Titration

2.870.1010	870 KF Titrino plus komplett
2.890.0110	890 Titrand including 803 Ti-Stand and Touch Control
2.901.0010	901 Titrand including titration cell and indicator electrode

Coulometric and volumetric KF titration

2.852.0050	852 Titrand including generator electrode with diaphragm and 801 Magnetic Stirrer
2.915.0110	915 Ti-Touch with integrated stirrer

KF Oven

2.874.0010	874 USB Oven Sample Processor
2.860.0010	860 KF Thermoprep
2.885.0010	885 Compact Oven Sample Changer

Oxidation stability

2.893.0010	893 Professional Biodiesel Rancimat including software and accessories
6.6068.102	StabNet 1.0 Full

Ion Chromatography

Glycerol in biodiesel

2.930.2160	930 Compact IC Flex
2.850.9110	IC Amperometric Detector
2.858.0020	858 Professional Sample Processor
6.1090.420	Metrosep Carb 2 - 150/4.0
6.5337.010	IC Equipment Wall-Jet cell: Carb (Au, Pd)

Alkali metals and alkaline earth metals in biodiesel

2.940.1110	940 Professional IC Vario ONE/Prep 1
2.858.0020	858 Professional Sample Processor – Pump
2.850.9010	IC Conductivity Detector
2.800.0010	800 Dosino
2.741.0010	741 Magnetic Stirrer
6.5330.120	IC equipment for dilution
6.5330.100	IC equipment for dialysis
6.2041.440	Sample rack 148 × 11 mL
6.1050.420	Metrosep C 4 - 150 /4.0
6.6059.312	MagIC Net 3.1 Professional



Antioxidants in biodiesel

2.930.2160	930 Compact IC Flex Oven/Deg
2.944.0010	944 Professional UV/VIS Detector Vario
2.858.0020	858 Professional Sample Processor – Pump
6.2041.440	Sample rack 148 × 11 mL
6.2061.120	System Connector
6.2061.110	Tray with sensor for Professional IC Instruments
6.6059.311	MagIC Net 3.1 Compact

Chloride and sulfate in ethanol

2.930.2560	930 Compact IC Flex Oven/SeS/PP/Deg
2.850.9010	IC Conductivity Detector
2.858.0020	858 Professional Sample Processor – Pump
6.2041.440	Sample rack 148 × 11 mL
6.5330.110	IC equipment for ultrafiltration
6.1006.530	Metrosep A Supp 5 - 250/4.0
6.2842.000	MSM-HC Rotor A
6.6059.311	MagIC Net 3.1 Compact

Sulfur content in fuel blends – Combustion IC

2.930.9010	930 Metrohm Combustion IC
6.1006.520	Metrosep A Supp 5 - 150/4.0

Voltammetry

2.884.0110	884 Professional VA (MME)
2.884.1110	884 Professional VA semiautomated MME consisting of 884 Professional VA, measuring head for MME, and two 800 Dosinos.
MVA-22	Fully automated Professional VA system consisting of 884 Professional VA, measuring head for the MME, 919 IC Autosampler plus for VA, and four 800 Dosinos for automatic addition of auxiliary solutions. Allows the automatic processing of up to 18 samples. This system is the optimum solution for automatic analysis of small sample series.
	Required accessories
6.5339.030	VA Electrode Kit 884 MME
6.6065.202	viva 2.0 Full

Process analysis

We offer online and atline Analyzers that meet any requirement in the process industry, from single-parameter to the most advanced multiparameter analyzers. Every analyzer is custom-tailored to the specific task at hand.

ADI2045PL	ProcessLab system for atline determination of various parameters using titration, colorimetry, and ISE
ADI 201Y Series	Single method Process Analyzers, available with titration, colorimetry, or ISE
ADI 204Y Series	Multifunctional Process Analyzers, available with titration, ISE, colorimetry, and voltammetry
2035 Series	Analyzer family designed in 3 configurations: potentiometric, photometric, and thermometric titration
ICON Analyzer	Analyzer from the Plug and Analyze Series that performs photometric absorption measurements
Alert Ion Analyzer	Analyzer from the Plug and Analyze Series that is used for measuring single parameters by ISE

Please contact your Metrohm supplier for further information. Please also consult www.metrohm.com



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