



Quality assurance of biofuels

- Determining the oxidation stability
- Water determination by Karl Fischer titration
- pH measurement and titrimetric analysis
- Ion chromatographic analysis

Biofuels in brief

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. However, 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 non-ferrous metals. A too high water content and the presence of alkali metal or alkaline earth metal ions as well as sulfate and chloride ions also have a negative effect on the fuel quality and can damage the fuel system of the vehicle. 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.

Several of the stipulated tests can be carried out with Metrohm instruments and Metrohm application methods.



Metrohm in the quality assurance of biofuels

If the standard is mentioned in the following table, this means that Metrohm instruments meet the stipulated minimum requirements for use in the standardized test method. The character «√» stands for a check of the quality criteria using a different testing method.

Page	Parameter	Biodiesel		Vegetable oil DIN V 51605	Bioethanol ASTM D 4806 ¹ ASTM D 5798 ²
		DIN EN 14214	ASTM 6751		
4 – 5	Oxidation stability	EN 14112	EN 14112	EN 14112	-
6 – 7	Water content KF _{coul.} Water content KF _{vol.}	EN ISO 12937	√	EN ISO 12937	ASTM E 1064 ASTM E 203
8 – 9	pH value	-	-	-	√
8 – 9	Chloride (potentiometric)	-	-	-	ASTM D 512 ASTM D 7xxx ³
8 – 9	Sulfate (potentiometric)	-	-	-	ASTM D 7xxx ³ ASTM D 6174
8 – 9	Acid number	EN 14104	ASTM D 664	EN 14104	ASTM D 1613
8 – 9	Iodine number	EN 14111	-	EN 14111	-
10 – 11	Chloride and Sulfate	-	-	-	ASTM D 7xxx ³
10 – 11	Alkali metals and alkaline earth metals	√	√	√	-
10 – 11	Antioxidants	recommended	-	recommended	-

¹ Standard specification for denatured alcohol that is added to fossil fuels.

² Standard specification for mixtures of bioethanol and gasoline (Ed75-Ed85).

³ Test method currently being evaluated in a round robin test.

The most important advantages at a glance

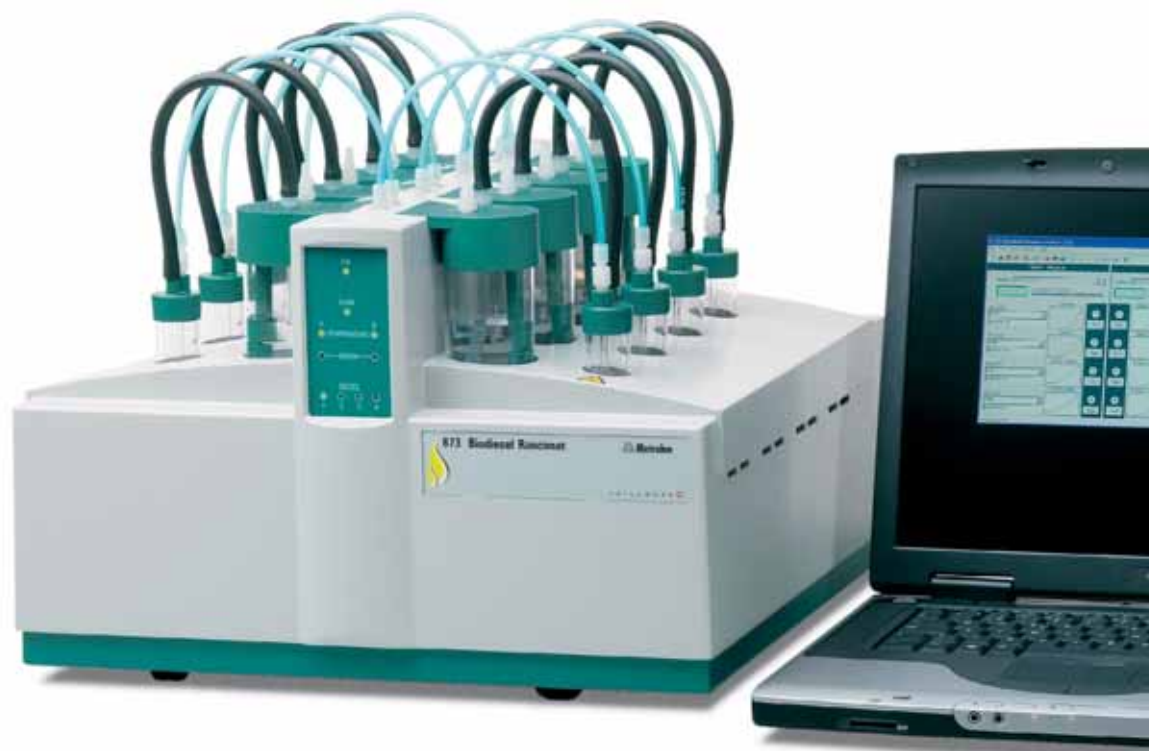
- Biofuel analysis from a single supplier
- Many years of application know-how in the ion analysis sector
- «Swiss made» technology for the determination of the biofuel quality parameters
- Three-year instrument warranty

Oxidation stability of fatty acid methyl esters (FAME) and vegetable oils as per EN 14112

873 Biodiesel Rancimat

Fatty acid methyl esters are usually obtained from oil seeds. During manufacture the vegetable oil is transesterified with methanol. This produces the methyl esters of the fatty acids present in the oil with glycerol as a byproduct. Vegetable oils and fatty acid methyl esters have a relatively short storage life as they are slowly oxidized by atmospheric oxygen. The resulting oxidation products can damage vehicle motors. 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. With the 873 Biodiesel Rancimat this determination can be carried out simply and reliably. The addition of suitable antioxidants slows down the oxidation process. The effectiveness of antioxidants can also be determined with the 873 Biodiesel Rancimat.

The 873 Biodiesel Rancimat is a modern, PC-controlled instrument for the convenient determination of the oxidation stability of oils and fats. The temperature can be set very accurately and reproducibly by using the GLP Set with certified temperature sensor; this further improves the precision of the results.





Reaction vessel

Disposable reaction vessels reduce the cleaning expenditure for accessories to an absolute minimum. This saves both time and costs. In addition, the accuracy and precision of the measurements is significantly improved.



Measuring cell

The conductivity electrode is built into the measuring cell cover. Easily breakable glass conductivity electrodes belong to the past. The built-in conductivity cell makes tedious cabling unnecessary. The measuring cell is extremely robust and easy to clean, which simplifies handling even more.



Software functions

All the functions of the third Rancimat generation are controlled by the Rancimat software, which is clearly laid out in only a few windows. Operation is intuitive and therefore extremely user-friendly. With automatic data acquisition and evaluation as well as a measurement database, the Rancimat software permits the comfortable management of large amounts of data.



Water determination by Karl Fischer titration

Water content of biodiesel

The water content of biodiesel determines the calorific value and, above all, the storage life of the fuel. Biodiesel with a high water content has a clearly lower oxidation stability. The lower the oxidation stability, the greater the probability that oxidation products will be formed during a longer storage period. These could damage the motor, in particular the fuel injection system, by forming deposits. In order to avoid this, DIN EN 14 214 limits the water content of biodiesel to 500 ppm.

The ISO standard 12 937 «Petroleum products – Determination of water – Coulometric Karl Fischer titration method» describes the coulometric Karl Fischer titration for determining the water content. The 756 and 831 KF 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. In order to improve the solubility of the samples, xylene (dimethylbenzene) is added to the KF reagent.

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 KF oven. The 832 KF Thermoprep oven 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 774 Oven Sample Processor.



831 KF Coulometer for determining trace amounts of water. The 756 KF Coulometer (not shown here) is additionally equipped with a built-in printer.

774 Oven Sample Processor with 831 KF Coulometer for the automatic determination of the water content in samples containing oil. Side-reactions and contamination of the KF coulometer cell no longer occur.

Water content of vegetable oils

Natural or simply filtered vegetable oils can also be used as a fuel for diesel motors. In contrast to biodiesel, which is obtained by chemically altering the vegetable oil and which can be used in standardized quality with existing motor technology, natural vegetable oils require adaptation of the diesel motor. As the presence of water favors the cleavage of fatty acids in the vegetable oil, standard DIN V 51 605 limits the permitted water content to 750 ppm.

The ISO standard 12 937 «Petroleum products – Determination of water – Coulometric Karl Fischer titration method» is also stipulated as a test method for vegetable oils. Because of the poor solubility of oils in methanol the use of a solubility promoter is also recommended here.

Water content in bioethanol

Bioethanol is mixed with gasoline in various ratios in order 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%.

The ASTM standard E 1064 «Standard Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration» describes 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 E 203. The volumetric KF titrators from Metrohm meet all the specifications required by the standard and are therefore extremely suitable for this application.



841 Titrando, the volumetric high-end titrator for demanding applications in KF titration.

pH measurement and titrimetric analysis



pH measurement

The pH value is an important quality criterion for all biofuels. A combined pH glass electrode with ground-joint diaphragm is recommended for measuring the pH in organic solvents. Because of the expected low conductivity of the sample, the electrode should be particularly well shielded in order to suppress electrostatic influences. The Solvotrode with separable ground-joint diaphragm is particularly suitable for measuring the pH of biofuels. 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.

Titrimetric determinations

• 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 14 104 stipulates a non-aqueous 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 (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 non-aqueous titrations. The separable ground-joint diaphragm guarantees stable potentials and is easy to clean.

• Iodine number in fatty acids and fatty acid methyl esters

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 is covered by European standard EN 14 111.

An aliquot of the biofuel sample is dissolved in a mixture of cyclohexane/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 14 111 allows both optical (with starch solution as the indicator) and potentiometric endpoint determination.

- *Chloride in bioethanol*

The chloride content in bioethanol fuels is the subject of ASTM D 512. 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).

- *Sulfate in bioethanol*

A proven method for sulfate determination is potentiometric titration with lead nitrate using a Pb-selective electrode. The pH 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 all-rounder
for potentiometric titration.**

The wide range of potentiometric applications for biofuels requires a highly flexible titrator. No other titration system offers more flexibility and working comfort than the Titrando.

- With Touch Control, the PC Control software or *tiamo™* – titration and more – operation is child's play.
- 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.



The Titrando offers maximum flexibility and operating comfort.

Ion chromatographic analysis

Ion chromatography for quality assurance

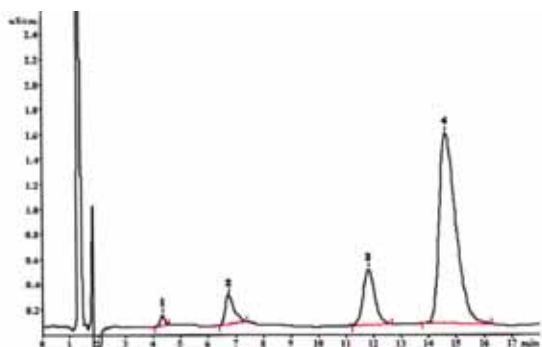
In addition to the determination of the oxidation stability, the water content and the acid and iodine numbers, the quality requirements for biofuels also cover limits for ionic species. Alkali metals and alkaline earth metals, antioxidants and anions such as chloride and sulfate can be determined by ion chromatography in order to check fulfillment of the requirements of DIN EN 14 214, DIN V 51 605 and ASTM D 4806 and therefore prevent motor damage.

Determining alkali metals and alkaline earth metals

After esterification and subsequent treatment, alkali metals and alkaline earth metals may be present in biodiesel as unwanted residues. They form salts with the anions contained in biodiesel and these block the fuel filter. In addition to this primary damage, secondary damage is caused to the injection pump. 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. This saves time and money.

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. The combination of instruments used consists of the 861 Advanced Compact IC with Metrohm inline extraction and dialysis. Both inline extraction and inline dialysis represent a form of the Metrohm Inline Sample Preparation «MISP».

Metrohm IC systems are characterized by their compact and robust design. The costs for consumables and reagents are reduced to a minimum. The complete system is PC-controlled. The IC Net software used can be understood intuitively and is therefore very user-friendly.



Biodiesel fuel; column: Metrosep C 2 – 150 (6.1010.220); eluent: 2 mmol/L HNO₃ + 10% acetone; flow: 1.0 mL/min; sample volume: 20 µL; peaks: 1. sodium 0.1 mg/L, 2. potassium 1.2 mg/L, 3. magnesium 0.7 mg/L, 4. calcium 5.0 mg/L.



861 Advanced Compact IC for fully automatic cation determination with Metrohm inline extraction and dialysis.

Determination of antioxidants

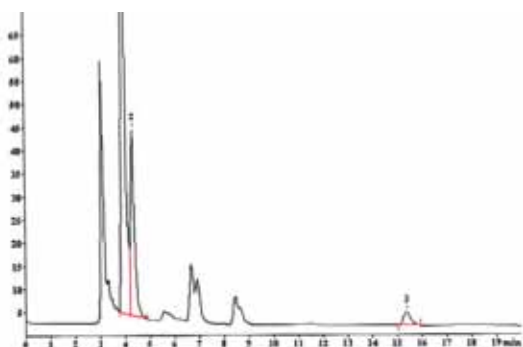
The oxidation stability of fatty acids and of the fatty acid methyl esters synthesized from them can be improved by the addition of antioxidants. Biodiesel based on rapeseed oil already contains an outstanding natural protection against oxidation – vitamin E (d- α -tocopherol). In addition Baynox[®], whose structure was inspired by that of vitamin E, is added to the biodiesel as a stabilizer. This inhibits both oxidation to corrosive acids and the formation of insoluble polymers and thus prevents the injection nozzles from being blocked. Both these substances are therefore determined within the context of quality monitoring and for determining the amounts of additives to be added.

Because of their structural similarities, vitamin E and Baynox[®] can be determined together in a single analysis. 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 then determined quantitatively using UV detection. For the determination of antioxidants for quality assurance purposes, Metrohm recommends the 844 UV/VIS Compact IC with built-in column heating. This unique instrument in the ion chromatography sector combines the advantages of a compact IC system with a diode array detector (DAD) in a single housing. The method can be completely automated by combination with the 838 Advanced Sample Processor. This saves both processing time and costs.

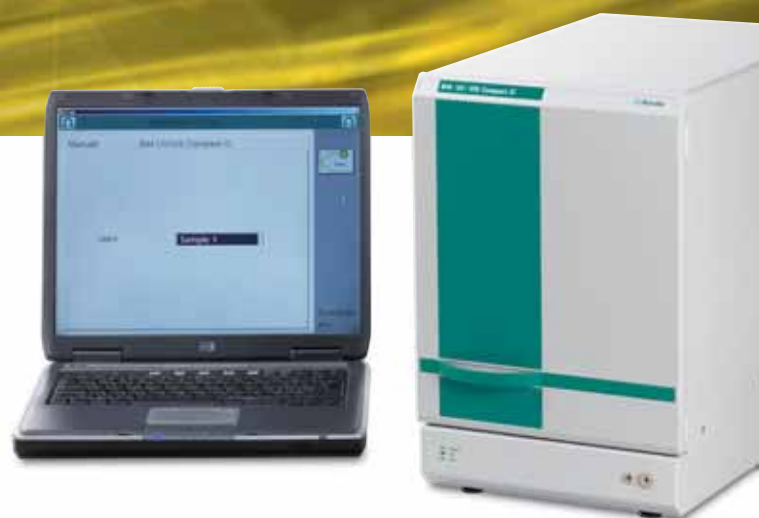
Chloride and sulfate

Bioethanol is either used in pure form as a fuel or mixed with fossil fuels. Contamination in the form of inorganic salts affects both the functioning and the working life of the motor. Against this background the ethanol specification ASTM D 4806 limits the sulfate content to 4 ppm and chloride to 40 ppm.

Chloride and sulfate are separated on an anion exchange column and then determined quantitatively by conductivity detection. The recommended setup is an 861 Advanced IC with Metrohm CO₂ Suppressor «MCS». The analysis can be completely automated by using an 838 Advanced IC Filtration Sample Processor, which allows inline ultrafiltration of the samples.



Biodiesel fuel spiked with 50 mg/L Baynox[®] and 5 mg/L α -tocopherol; column: Prontosil 120-5-C18-H; eluent: 90% acetonitrile + 10% dichloromethane; wavelength: 220 nm; flow: 1.0 mL/min; temperature: 35 °C; sample volume: 10 μ L; dilution: 1:1000; peaks: 2. Baynox[®] 50.2 mg/L, 3. α -tocopherol 4.9 mg/L.



844 UV/VIS Compact IC with built-in column heating.

Technical specifications and ordering information

• Determination of oxidation stability: 873 Biodiesel Rancimat

Technical specifications

Heating blocks	2
Temperature range	50...220 °C
Temperature variation	<0.1 °C
Number of samples	8 (4 per heating block)
Air throughput	7...25 L/h (membrane pump)
Conductivity measurement	0...400 µS/cm (double steel-pin electrode built into measuring vessel cover)

Ordering information

2.873.0014	873 Biodiesel Rancimat (230 V) with software and accessories
or	
2.873.0015	873 Biodiesel Rancimat (115 V) with software and accessories

Options

6.5616.000	GLP test set
6.1429.050	Reaction vessel long (length 250 mm) for measurements on volatile oils, mineral oils and biodiesel blends
6.2418.130	Air inlet tube long (length 248 mm) for measurements on volatile oils, mineral oils and biodiesel blends

Consumables

6.1428.030	Conductivity measuring vessel, glass
6.1429.040	Reaction vessels (117 pcs.)
6.2753.100	Reaction vessel cover
6.2418.100	Air inlet tubes (117 pcs.)
6.1839.000	Iso-Versinic® tubing

• Water determination by Karl Fischer titration

Technical specifications

Determination range	10 µg...200 mg H ₂ O (coulometric) 100 ppm...100% H ₂ O (volumetric)
774 Oven Sample Processor	
Temperature range	50...250 °C
Capacity	35 samples plus 1 conditioning vessel

Ordering information

Coulometric KF titration

2.831.0010	KF Coulometer including titration cell with diaphragm and 728 Magnetic Stirrer
or	
2.756.0010	KF Coulometer including titration cell with diaphragm, 728 Magnetic Stirrer and built-in printer

Volumetric KF titration

2.841.0010	Titrande with titration cell and indicator electrode
2.840.0100	Touch Control
2.803.0010	Ti Stand
2.800.0010	Dosino
6.3032.210	Dosing Unit 10 mL (titrant)

KF Oven

2.774.0010	Oven Sample Processor
2.832.0020	Thermoprep

• pH measurement and titrimetric analysis

pH measurement

Ordering information

2.827.011X	827 pH lab, X = 4 (EU), X = 5 (US), X = 7 (AUS), X = 9 (UK)
2.826.0010	826 pH mobile
6.0229.100	LL Solvotrode
6.2104.020	Electrode cable
6.2312.010	Electrolyte LiCl = 2 mol/L in ethanol (250 mL)

Titrimetric analysis

Technical specifications

Titrando

Universal titrator for up to four 800 Dosino dosing systems. Dynamic (DET) and monotonic (MET) titration, endpoint titration (SET), volumetric KF titration (835 and 836 Titrandos), measurement with ion-selective electrodes (MEAS CONC), dosing functions with monitoring (DOS), liquid handling. With four MSB connections, one or two electrically isolated measuring interfaces, 2 USB slave ports for connection to balance, printer, PC or barcode reader.

Ordering information

Acid number

2.809.0010	Titrando
2.840.0100	Touch Control
2.801.0040	Magnetic Stirrer
2.800.0010	Dosino (2 pcs. for adding titrant and solvent)
6.3032.220	Dosing Unit 20 mL (titrant)
6.3032.250	Dosing Unit 50 mL (solvent)
6.0229.100	Solvotrode (pH measurement)
6.2320.000	Electrolyte TEABr = 0.4 mol/L in ethylene glycol

Iodine number

2.809.0010	Titrando
2.840.0100	Touch Control
2.801.0040	Magnetic Stirrer
2.800.0010	Dosino
6.3032.220	Dosing Unit 20 mL (titrant)
6.0431.100	Pt Titrode (iodine number)

Chloride in bioethanol

2.809.0010	Titrando
2.840.0100	Touch Control
2.801.0040	Magnetic Stirrer
2.800.0010	Dosino (2 pcs. for adding titrant and nitric acid)
6.3032.220	Dosing Unit 20 mL (titrant)
6.3032.210	Dosing Unit 10 mL (nitric acid)
6.0430.100	Ag Titrode (chloride)

Sulfate in bioethanol

2.809.0010	Titrando
2.840.0100	Touch Control
2.801.0040	Magnetic Stirrer
2.800.0010	Dosino (2 pcs. for adding 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

• Ion chromatographic analysis

Technical specifications

Pump	low-pulsation serial double-piston pump, flow range 0.2...2.5 mL/min
Column heating	for 2 columns – range: ambient temperature +5 °C...80 °C
Suppressors (IC 861)	Metrohm Suppressor Module «MSM II» (with 10-year warranty) and Metrohm CO ₂ Suppressor «MCS»
Detector (IC 861)	conductivity detector, 4 measuring ranges 0...50 µS/cm, 0...250 µS/cm, 0...1000 µS/cm, 0...5000 µS/cm
Detector (IC 844)	diode array detector «DAD», 3 wavelengths, measuring range 190...900 nm

Ordering information

Alkali metal and alkaline earth metal determination

2.861.0010	861 Advanced Compact IC (including IC Net software)
2.838.0120	838 Advanced IC Dilution Sample Processor
2.833.0040	833 Advanced IC Liquid Handling Dialysis Unit
2.800.0010	800 Dosino
2.801.0010	801 Magnetic Stirrer
2.772.0110	772 Pump Unit
6.1562.130	Transfer tubing 10 mL
6.3032.210	Dosing Unit 10 mL
6.1010.220	Metrosep C 2 – 150
6.1010.200	Metrosep C 2 Guard
6.2041.440	Sample Rack 148 x 11 mL

Antioxidant determination

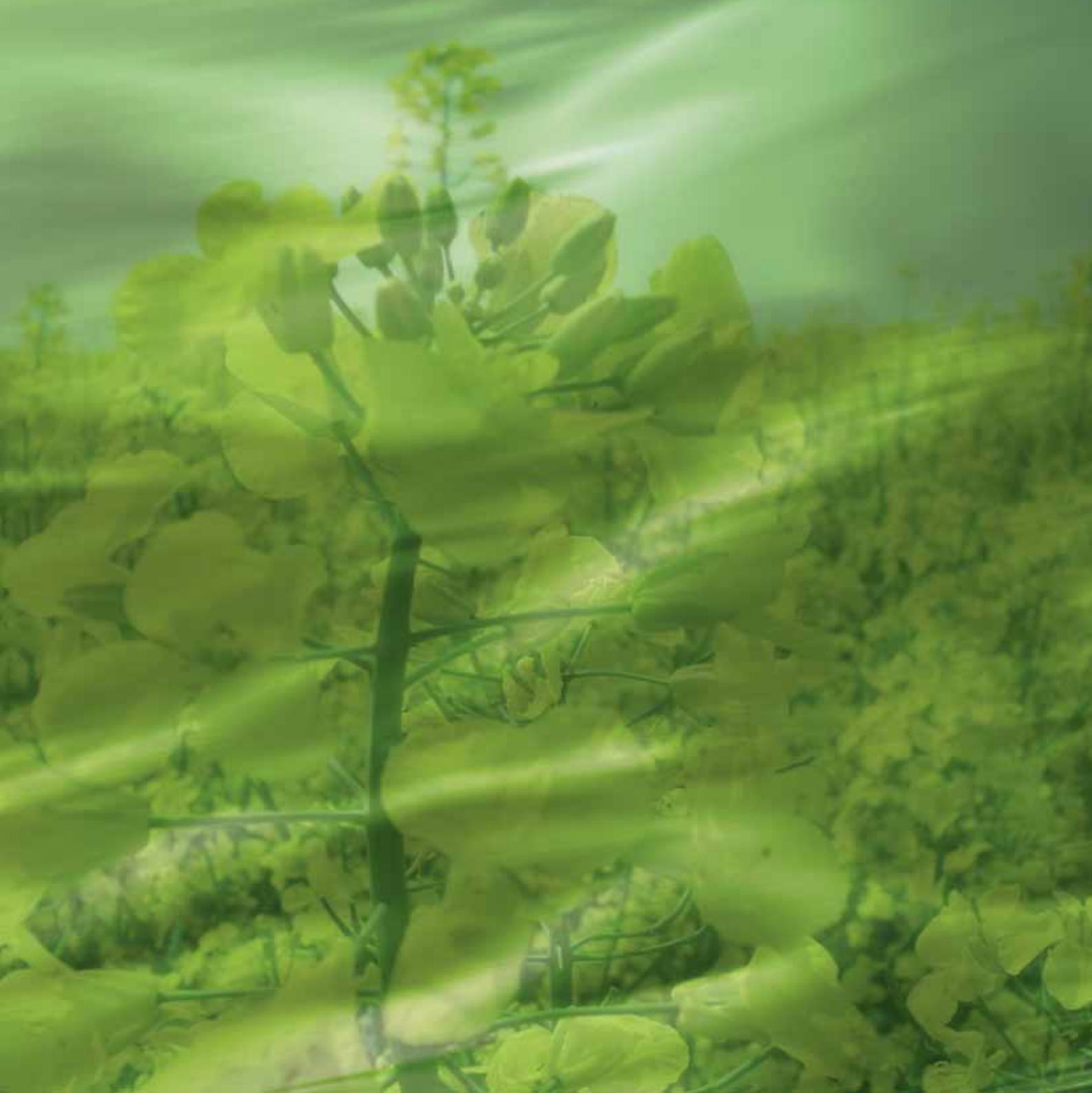
2.844.0110	844 UV/VIS Compact IC with built-in column heating (including IC Net software)
2.838.0010	838 Advanced IC Sample Processor
6.2041.440	Sample Rack 148 x 11 mL

Chloride and sulfate determination

2.861.0040	861 Advanced Compact IC (including IC Net software)
2.838.0210	838 Advanced IC Filtration Sample Processor
6.1006.530	Metrosep A Supp 5 – 250
6.1006.500	Metrosep A Supp 4/5 Guard
6.2041.440	Sample Rack 148 x 11 mL

Options

2.837.0010	837 IC Eluent Degasser
2.845.0020	845 Eluent Synthesizer
2.861.0500	Column heating for 861 Advanced Compact IC
6.2743.050	Sample vessels 11 mL (2000 pcs.)
6.2743.070	PP stoppers with perforation, for sealing sample vessels (2000 pcs.)





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Ion analysis

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s w i s s m a d e 