

Petrochemical analysis



Quality control of petroleum products



Metrohm ...

- is the global market leader in titration
- is the only company to offer a complete range of ion analysis equipment – 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 ion chromatography
- provides you with unparalleled application expertise
- offers you more than 1300 applications free of charge
- supports you with expert service through local representatives and regional support centers
- is not listed on the stock exchange, but is owned by a foundation
- gives the interest of customers and employees priority over maximizing profit

Metrohm – customized analysis for the petrochemical industry

A demanding industry

It is a long way from crude oil to the innumerable products made from it. The industrial refining processes are demanding.

As a leading solution provider to the petrochemical industry, we are quite aware of these challenges. We offer you state-of-the-art instrumentation helping you to check and improve the quality of petrochemical products and 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 petrochemical industry in general and you in particular, to ensure the quality and safety of your products.



Analysis of petroleum products

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Formation of crude oil deposits

According to current knowledge our oil reserves originated during the Jurassic and Cretaceous periods (200 to 65 million years ago) from microbial flora and fauna living in the seas. While some of the dead organic residues were directly mineralized, i.e. decomposed, the other part sank to the seabed. There the material was covered by other marine deposits and formed a sludge with very fine rock material that slowly converted to crude oil under the prevailing biogeochemical conditions of increased pressure and salinity. Due to its lower density the crude oil migrated upwards through fine cracks in the rock layers until it accumulated under impermeable covering rocks and thus formed the oil deposits we know today. Sometimes above-ground oil deposits were formed that already allowed our forefathers to use crude oil for heating and lighting, building, or lubrication.

«Lubricant» of the global economy

Nowadays crude oil, which consists of at least 500 different components, is processed by distillation and refining to liquid gas, gasoline, diesel, and heating fuel, lubricants as well as a large variety of other products. As the «lubricant» of the global economy, crude oil is omnipresent. It covers approximately 40% of our energy demand and is used in the chemical industry for the production of plastics, textiles, and dyes, cosmetics, fertilizers, detergents, building materials, and pharmaceuticals.

The importance of the petroleum products and their derivatives is reflected by the large number of standards relating to them. Metrohm as a leading manufacturer of instruments for ion analysis offers long-standing application know-how for the quality assurance of petroleum products.



Selected standards from the field of petrochemical analysis

The standards listed below describe numerous international testing and requirement specifications for petroleum products. Metrohm instruments comply with all the minimum requirements and limits stipulated by the respective standards.

Parameter	Standard	Matrix	Method	Page	
Base number	ASTM D 4739	Petroleum products Lubricants	Potentiometric titration	6	
	ASTM D 2896	Petroleum products	Potentiometric titration		
Total base number	DIN ISO 3771	Petroleum products	Potentiometric titration		
Nitrogenous bases	UOP269	Petroleum distillates	Potentiometric titration		
Acid and base number	ASTM D 974	Petroleum products	Colorimetric titration		
	ASTM D 664	Petroleum products	Potentiometric titration		
Acid number	DIN EN 12634	Petroleum products Lubricants	Potentiometric titration		
	UOP565	Petroleum products Petroleum distillates	Potentiometric titration		
Mercaptan sulfur	ASTM D 3227	Automotive fuel, kerosene	Potentiometric titration		8
	ISO 3012	Highly volatile distillates Moderately volatile distillates	Potentiometric titration		
H ₂ S	ASTM D 2420	Liquefied petroleum gas (LPG)	Potentiometric titration		
H ₂ S, mercaptan sulfur	UOP163	Petroleum products	Potentiometric titration		
Alkalinity, H ₂ S, mercaptans	UOP209	Used alkaline petroleum products	Potentiometric titration		
H ₂ S, mercaptan sulfur, carbonyl sulfide	UOP212	Gaseous hydrocarbons Liquefied petroleum gas (LPG)	Potentiometric titration		
Saponification number	ASTM D 94	Petroleum products	Potentiometric titration	9	
	DIN 51559	Crude oil Insulating oil	Colorimetric titration		
Bromine number	ASTM D 1159	Petroleum distillates Aliphatic alkenes	Potentiometric titration	10	
	ASTM D 5776	Aromatic hydrocarbons	Potentiometric titration		
	ISO 3839	Petroleum distillates Alkenes	Potentiometric titration		
Bromine number and bromine index	UOP304	Hydrocarbons	Potentiometric titration		
Bromine index	ASTM D 2710	Petroleum hydrocarbons	Potentiometric titration		
Hydroxyl number	ASTM E 1899	Aliphatic and cyclic hydrocarbons	Potentiometric titration	10	
	DIN 53240	Resins, raw materials for varnishes, primary alcohols, glycols, fat	Potentiometric titration		
Organic, inorganic and total chlorine content	UOP588	Hydrocarbons	Potentiometric titration	11	
Organic chlorine content	ASTM D 4929	Crude oil	Potentiometric titration	11	
Salinity	ASTM D 6470	Crude oil	Potentiometric titration	12	
	DIN 51777-1/2 ^a	Petroleum hydrocarbons Solvents	Coulometric KFT ^b Volumetric KFT		
	ASTM D 4377	Crude oil	Volumetric KFT		
	ASTM D 4928	Crude oil	Coulometric KFT		
	ASTM E 1064	Crude oil Organic solvents Lubricating oil	Coulometric KFT		
	ASTM D 6304	Petroleum products	Coulometric KFT		
	ASTM D 1364	Highly volatile solvents	Volumetric KFT		
	ASTM D 890	Turpentine	Azeotropic distillation, KFT		
	ASTM E 203	General	Volumetric KFT		
	ISO 10336	Crude oil	Volumetric KFT		
ISO 10337	Crude oil	Coulometric KFT			
ISO 12937	Petroleum products	Coulometric KFT			
ISO 6296	Petroleum products	Volumetric KFT			
Oxidation stability	EN 14112	Fatty acid methyl esters (B100)	Oxidation stability	14	
	EN 15751	Fatty acid methyl esters Diesel fuel blends	Oxidation stability		
Inorganic chloride and sulfate	DIN EN 15492, ASTM D 7319, ASTM D 7328	Ethanol as a blending component in gasoline	Ion chromatography	16	
Free and total glycerol content ^c	ASTM D 7591	Biodiesel blends	Ion chromatography	16	
Sulfur, heavy metals	–	Gasoline, ethanol	Voltammetry	22	
pH value, conductivity, and parameters that can be determined by titration and voltammetry	Process-dependent conditions	Petroleum products	Process analysis	24	

^ain revision, ^bKarl Fischer titration, ^cTest methods for the biofuel sector can be found in the brochure «Biofuel analysis» (8.000.5013EN).

Determination of acid and base numbers

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Potentiometric titration with the Solvotrode

With the base number, alkaline components are determined in petroleum products as a sum parameter. These include primary organic and inorganic amino compounds in particular. However, salts of weak acids, basic salts of polycarboxylic acids, a number of heavy metal salts, and detergents are also recorded. The base number indicates how many basic components, expressed as mg KOH, are contained in 1 g of sample. This determination is used for the immediate detection of product changes during use.

With the acid number, acidic components are measured in petroleum products as a sum parameter. These are compounds (acids, salts) with pK_s values < 9 . The acid number indicates how many mg KOH are required to neutralize 1 g of sample. The acid number indicates changes during the use of the product. Both parameters are determined by potentiometric titration in nonaqueous solvents or solvent mixtures. Titrimetric determinations can be completely automated – from the addition of solvents to the cleaning of the electrode. Oil samples can even be weighed in fully automatically by the 864 Robotic Balance Sample Processor before titration. This guarantees complete traceability.

The Solvotrode easyClean is a combined pH glass electrode that was especially developed for this application. The separable ground-joint diaphragm can be easily cleaned even of strong contamination. The electrostatic shielding of the electrolyte compartment also ensures a low-noise measuring signal.



Solvotrode easyClean

Determination of acid and base number according to ASTM D 974 (photometric detection)

The acid and base number may also be determined in a photometric titration with color indication of the equivalence point according to ASTM D 974. For this application, Metrohm offers the Optrode, a new sensor for photometric titration. It is 100% solvent resistant (glass shaft) and – unlike visual endpoint recognition – enables automation of the determination.



Optrode

Standard	Parameter	Titrant	Solvent	Electrode (reference electrolyte)
ASTM D 4739	Base number	HCl in isopropanol	Chloroform, toluene, isopropanol, water	Solvotrode easyClean (LiCl in EtOH)
ASTM D 2896	Base number >300 mg KOH/g	Perchloric acid in glacial acetic acid	Glacial acetic acid, xylene	Solvotrode easyClean (TEABr ^a in ethylene glycol)
DIN ISO 3771	Total base number	Perchloric acid in glacial acetic acid	Toluene, glacial acetic acid, acetone	Solvotrode easyClean (TEABr in ethylene glycol)
ASTM D 664	Acid number	KOH in isopropanol	Toluene, isopropanol, water (lubricants) Isopropanol (biodiesel)	Solvotrode easyClean (LiCl in EtOH)
DIN EN 12634	Acid number	KOH in TMAH ^b	Dimethylsulfoxide, isopropanol, toluene	Solvotrode easyClean (LiCl in EtOH)
UOP565	Acid number and naphthenic acids	KOH in isopropanol	Toluene, isopropanol, water	Solvotrode easyClean (LiCl in EtOH)
ASTM D 974	Acid Number	KOH in isopropanol	Toluene/isopropanol/water	Optrode
ASTM D 974	Base Number	HCl in isopropanol	Toluene/isopropanol/water	Optrode

^a Tetraethylammonium bromide

^b Tetramethylammonium hydroxide



855 Robotic Titrosampler (with 772 Pump Unit) for TAN/TBN determination

Sulfur and sulfur compounds determined by potentiometric titration with the Ag-Titrode

Sulfur compounds contained in petroleum products not only have an unpleasant odor, they are also environmentally damaging and promote corrosion. For determining hydrogen sulfide and mercaptans in liquid hydrocarbons (gasoline, kerosene, naphtha, and similar distillates), the sample is titrated with silver nitrate solution, whereby silver sulfide (Ag_2S) and silver mercaptide are produced. Two pronounced potential jumps occur. The first endpoint corresponds to hydrogen sulfide (H_2S), the second to the mercaptans. The indicator electrode for the titration is the Ag-Titrode, version with Ag_2S coating. Since both H_2S and mercaptans are oxidized by atmospheric oxygen and the arising oxidation products cannot be determined titrimetrically, work must be carried out under a nitrogen atmosphere.

Gaseous sulfur compounds can also be determined with this procedure. For this purpose, they are absorbed in an alkaline solution. The first two absorption vessels contain KOH or NaOH (for H_2S and mercaptans), the third contains ethanolic monoethanolamine (for carbonyl sulfide).

The results are expressed in mg/kg (ppm) hydrogen sulfide and/or mercaptan sulfur.

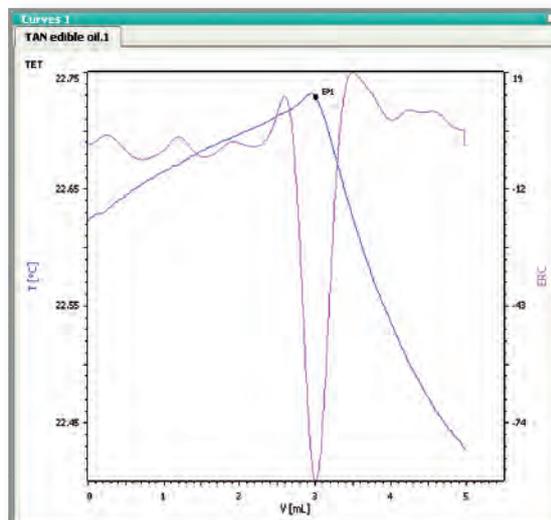


Thermometric titration

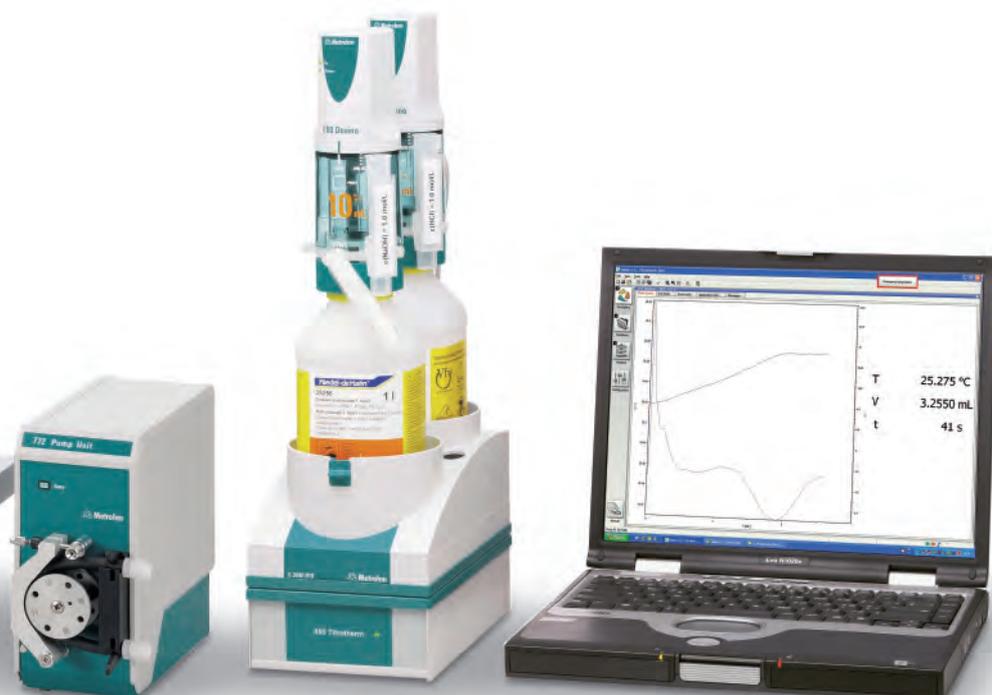
Instrumental methods using a glass-membrane pH electrode suffer from the difficulty of working in a water-free environment of very low electrical conductivity where the glass membrane is rapidly dehydrated or the sensor is contaminated by the sample. This results in a need for time-consuming sensor maintenance, which has to be carried out with high reproducibility.

Similarly, the determination of TBN involves a nonaqueous titration of the weakly basic substances contained in the additive packages using strong acids diluted in suitable solvents. Typically, perchloric acid in glacial acetic acid is used as the titrant. Glass membrane potentiometric sensors suffer similar problems in the determination of TBN as during the TAN determination.

The alternative thermometric titration procedure overcomes the above mentioned problems. It is based on the principle, that every chemical reaction is accompanied by a change in enthalpy (ΔH). As long as the reaction takes place, this results in either an increase (exothermic reaction) or decrease (endothermic reaction) in the temperature of the sample solution, which is indicated by a very sensitive temperature sensor. For TAN and TBN, this is enhanced by the use of special chemical thermometric indicators. The method can also be fully automated and titration times are approximately three times faster than their potentiometric titration counterparts. Less solvent and no special sensor maintenance is required.



Catalytically enhanced thermometric titration: after the endpoint has been reached, the excess hydroxide ions catalyze the endothermic hydrolysis of the added paraformaldehyde.



Saponification number

The saponification number (SN) primarily serves to determine the proportion of fatty acid esters in the sample. The fatty acid esters are cleaved by boiling in KOH, a process which produces the salts of the fatty acids and the corresponding alcohol, for example, glycerol. The method is not specific since acidic sample constituents consume KOH and in so doing increase the saponification number (SN). The titrant employed is $c(\text{HCl}) = 0.5 \text{ mol/L}$ in isopropanol. The SN indicates how many mg KOH are consumed by 1 g sample under the test conditions.

Bromine number and bromine index

The bromine number (BN) and the bromine index (BI) indicate the proportion of unsaturated compounds (usually C-C double bonds) in petroleum products. Here, the double bond is cleaved by bromine addition. The BN indicates how many g of bromine (Br_2) are bound by 100 g of sample.

The method is used for the following products:

- Distillates with a boiling point below $327 \text{ }^\circ\text{C}$ ($620 \text{ }^\circ\text{F}$) and a volume percentage of at least 90% of compounds that are lighter than 2-methylpropane (included in this are fuels with and without lead additions, kerosene and gas oils).
- Commercial alkenes (mixtures of aliphatic monoalkenes) with a bromine number from 95 to 165.
- Propenes (trimers and tetramers), butene trimers, mixtures of nonenes, octenes, and heptenes.

The BI indicates how many mg of bromine (Br_2) are bound by 100 g of sample. The method is used for «alkene-free» hydrocarbons with a boiling point below $288 \text{ }^\circ\text{C}$ ($550 \text{ }^\circ\text{F}$) and a bromine index of between 100 and 1000. For products with a bromine index of >1000 the bromine number should be used.

Method	Samples	Titrant	Solvent	Electrode
Bromine number [g Br_2 /100 g]	Automotive fuels, kerosene, gas oils, propene, butenes, heptenes, octenes, nonenes	$c(\text{bromide}/\text{bromate solution}) = 0.08333 \text{ mol/L}$	Glacial acetic acid, trichloroethane, methanol	Double Pt-wire electrode
Bromine index [mg Br_2 /100 g]	Olefin-free hydrocarbons	$c(\text{bromide}/\text{bromate solution}) = 0.00333 \text{ mol/L}$	Glacial acetic acid, trichloroethane, methanol	Double Pt-wire electrode





Hydroxyl number

The hydroxyl number (OHN) indicates the number of mg KOH corresponding to the hydroxyl groups in 1 g sample. The most frequently described method for determining the hydroxyl number is conversion of the sample with acetic acid anhydride in pyridine with subsequent titration of the released acetic acid. The one-hour boiling under reflux, the difficulty in automating the process and particularly the use of the health-hazardous pyridine are serious disadvantages.

An alternative is offered by the considerably simpler and more easily automated method according to ASTM E 1899. Primary and secondary hydroxyl groups are converted with toluene-4-sulfonyl-isocyanate (TSI) into an acid carbamate, which is then titrated with the strong base tetrabutylammonium hydroxide (TBAH) in a non-aqueous medium. The method is especially suitable for neutral raffinates. Acidic products can falsely indicate too high values. In the same way products that contain bases can show too low values due to neutralization of the carbamate formed.

In comparison to the formerly used 1-hour boiling under reflux, this automated procedure is much more time saving, convenient, and reproducible, as it guarantees that every sample is treated in exactly the same way.

Chloride and organically bound chlorine

Organically bound chlorine present in petroleum products is decomposed at high temperatures and forms hydrochloric acid, which is highly corrosive and can cause damage, for example, to the distillation columns.

Before measurement, the sample is freed of sulfur compounds and inorganic chlorides by distillation and subsequent washing as described in ASTM D 4929. The organically bound chlorine is converted to NaCl with metallic sodium in toluene. After extraction into the aqueous phase the NaCl is titrated potentiometrically with silver nitrate solution.

Water determination according to Karl Fischer

Water occurs as a contaminant in virtually all petroleum products. It reduces lubricant properties, promotes microbial oil degradation, leads to sludge formation in the tank, and promotes corrosion of ferrous and nonferrous metals. While at higher temperatures water boils and contributes to a partial degreasing, temperatures below freezing point lead to the formation of ice crystals and a rapid decrease in lubricity. In addition, insulating and transformer oils used in high-voltage engineering become electrically conducting and are therefore rendered useless in the presence of water.

In view of this, knowledge of the water content in petroleum products is of prime importance. Karl Fischer titration, owing to its excellent reproducibility and accuracy as well as its ease of use, numbers amongst the most important water determination methods and accordingly figures in numerous international standards. Measurement can occur by volumetric or coulometric Karl Fischer titration. Because of the low water content in petroleum products, KF coulometry is usually applied.

Aliphatic and aromatic petroleum components

Water determination in these products is simple. They usually contain only little water so that the coulometric Karl Fischer titration is used. If volumetric titration has to be carried out, reagents with a low titer must be used. For long-chain hydrocarbons, the addition of a solubilizer (propanol, decanol or chloroform) is recommended to improve solubility. In the rare case of interferences by double bonds, the use of one-component reagents is recommended.

Hydraulics, insulation, transformer and turbine oils

In these oils the water content is almost always determined coulometrically using a diaphragm cell. Due to the poor solubility in methanol, solubilizers must be used (chloroform or trichloroethylene). Since these products feature a very low water content, it is very important to achieve a low and constant drift value.

Engine oils, lubricating oils, and lubricating greases

The additives frequently present in these oil samples can react with KF reagents and falsify the result. If a KF drying oven is used, a stream of dry carrier gas transfers the expelled water into the titration cell. Since the sample itself does not come into contact with the KF reagent, interfering side reactions and matrix effects can be excluded. The correct heating temperature lies below the decomposition temperature of the sample and is determined in preliminary tests.

Turpentine and its distillation products

After addition of toluene or xylene, the water is transferred by azeotropic distillation to the titration cell where it is determined by Karl Fischer titration.



KF Evaporator



860 KF Thermoprep with 851 Titrando



Petroleum (crude oil, heavy oil)

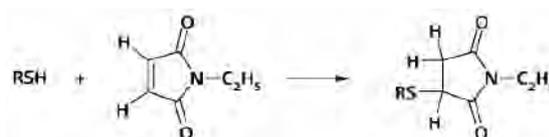
Water is not homogeneously distributed in these products, so that the petroleum samples must first be homogenized before analysis, for example, with the Polytron PT 1300D. Furthermore, crude and heavy oils contain tars that can seriously contaminate electrodes and titration cells. Reagents must therefore be exchanged regularly and the titration cells must be cleaned frequently. In order to ensure that the sample completely dissolves, solubilizers are added to the methanol:

- Crude oil (in general) 10 mL methanol + 10 mL chloroform + 10 mL toluene
- Heavy oil 10 mL methanol + 10 mL chloroform + 20 mL toluene

Fuels

This group contains mercaptans that are oxidized by iodine and thus produce too high water contents. The problem is dealt with by adding N-ethylmaleimide, which causes the SH groups of the mercaptan to attach themselves to the double bond of the N-ethylmaleimide.

Another option is the separate determination of the mercaptan component by potentiometric titration with silver nitrate. The result of the water determination reduced by this amount corresponds to the actual water content of the sample (1 ppm mercaptan sulfur corresponds to approx. 0.5 ppm water). Normally the water content in fuels is determined by coulometric titration. With volumetric titration a solubilizer must be added to the methanol.



Reaction of a mercaptane with N-ethylmaleimide

Mobile coulometry with the 899 Coulometer

There are situations where a quick determination of the water content is required but the laboratory is far and waiting for results is out of the question. There might be no socket around to plug in a power cord either. For situations like this, the compact 899 Coulometer comes with an optional Power Box. It contains a set of rechargeable batteries lasting for hours of uninterrupted operation.



899 Coulometer and optional Power Box

Oxidation stability

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If stored in such a way that air has access, petroleum undergoes oxidizing reactions whose reaction products can lead to problems in combustion engines. Polymers and poorly soluble compounds in particular lead to deposits in and blockages of the fuel injector systems. The aging behavior (oxidation stability) is therefore a very important property of petroleum products.

In order to quantitatively determine the oxidation stability using the Rancimat method, air is passed through the sample to be examined at an elevated temperature to bring about artificial aging. During this process long-chain organic molecules are oxidized by oxygen, whereby highly volatile organic substances form in addition to insoluble polymer compounds. The former are

driven out by the air current, absorbed in water and detected there by measuring the conductivity. The time until formation of these decomposition products occurs is referred to as the induction time or the Oil Stability Index (OSI) and characterizes the resistance of the sample towards oxidative aging processes, i.e. the oxidation stability.

873 Biodiesel Rancimat

The 873 Biodiesel Rancimat allows the simple and reliable determination of oxidation stability in petroleum products and biodiesel. The device is controlled via a PC; the PC software records the measurement curves, automatically evaluating them and calculating the result. Up to eight samples can be measured simultaneously.





Important applications

Biodiesel and biodiesel blends

Biodiesel (FAME, fatty acid methyl esters) is usually extracted from oilseeds by transesterification with methanol. It is being added more and more to mineral diesel as a blending component. Vegetable oils and methyl esters of fatty acids are relatively unstable under storage conditions since they are slowly oxidized by atmospheric oxygen. Just as with oxidation of petroleum, polymer compounds are formed during the oxidizing of biodiesel that can cause damage to engines. For this reason, oxidation stability is an important quality criterion for biodiesel and vegetable oils that must be controlled regularly during production according to EN 14112. The corresponding method for biodiesel blends is described in EN 15751. The addition of suitable antioxidants slows down the oxidation process. The 873 Biodiesel Rancimat also allows to determine the effectiveness of antioxidants.

Ultra-low sulfur diesel fuel

As a result of environmental protection concerns and technical requirements for motor vehicle manufacturers, sulfur-

free diesel fuel is appearing more and more on the market (ultra-low-sulfur diesel). This mineral diesel fuel with a sulfur content of at most 10 ppm (EU) or 15 ppm (USA) is oxidized considerably more easily than the formerly used diesel fuels with a higher sulfur content. This means that oxidation stability has also become an important parameter for fuel production. The 873 Biodiesel Rancimat allows a simple assessment of oxidation stability.

Biologically easily degradable lubricating oils

Biologically easily degradable lubricants can also be manufactured from natural fat and oils. Like the raw material, these products are also susceptible to oxidation.

Heating oil

Alongside other methods the Rancimat method is also used for assessing the oxidation stability of light fuel oil. In order to accelerate the reaction, metallic copper is added to the fuel oil sample to act as a catalyst.



Ion chromatographic analyses

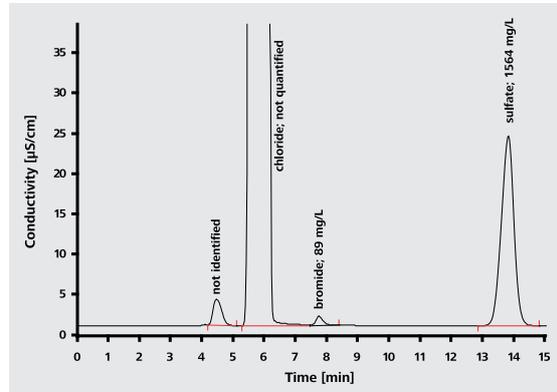
The quality assurance of petroleum products involves numerous applications of ion chromatography in which inorganic and low-molecular organic ions are determined in fuels, lubricating oils, gas-washing solutions and the so-called «Produced water» that is a by-product of crude oil drilling.

Anions and cations in «Produced water»

During oil production large quantities of «Produced water» are transported to the surface. In addition to oil drops and dissolved organic components, «Produced water» contains large amounts of inorganic cations such as calcium, magnesium, barium, and strontium as well as anions such as carbonate, bromide, and sulfate. The resulting salts can cause scaling and ultimately block the piping. For this reason, the determination of inorganic components is of essential importance, last but not least also for the correct dosing of scale inhibitors.



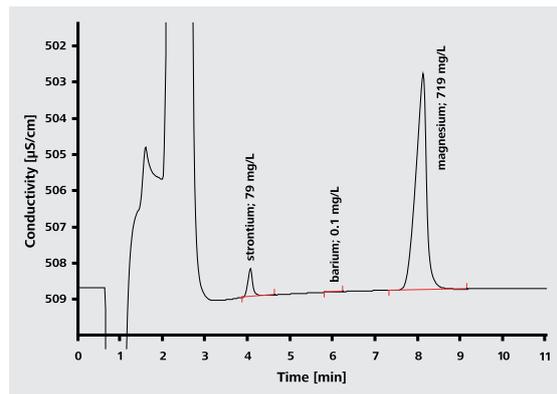
Since determinations occur not only on-shore, but also off-shore, robust analytical devices that do not need to be serviced frequently are required. This is offered by the 881 Compact IC pro in combination with the 858 Professional Sample Processor. The system can also be equipped with the inline dialysis system patented by Metrohm. The intelligent chromatography software MagIC Net™ assumes control of the device, the data management and the system monitoring and can, if necessary, be configured as «One-button IC» for semi-skilled personnel.



Anions in «Produced water»; column: Metrosep A Supp 4 - 250/4.0 (6.1006.430); eluent: 1.8 mmol/L Na_2CO_3 , 1.7 mmol/L NaHCO_3 , 1.0 mL/min; sample volume: 20 μL ; sample dilution 1:20



881 Compact IC pro in combination with 858 Professional Sample Processor, optionally equipped with inline dialysis



Cations in «Produced water»; column: Nucleosil 5SA - 125/4.0 (6.1007.000); eluent: 4.0 mmol/L tartaric acid, 3.0 mmol/L ethylenediamine, 0.5 mmol/L dipicolinic acid, 5% acetone, 1.5 mL/min; sample volume: 20 μL ; sample dilution 1:10



Anions in gasoline-ethanol blends

The use of energy from renewable sources and the associated reduction of greenhouse gases is one of the most pressing goals of our modern industrial society. Ethanol manufactured from waste and renewable plant material, which can be mixed with conventional gasoline in any proportion, is regarded as one of the most promising alternatives. Contaminants in the form of inorganic salts, however, impair engine performance, so that various international standards now regulate particularly the chloride and sulfate content of gasoline-ethanol blends.

Additional IC applications for petrochemistry

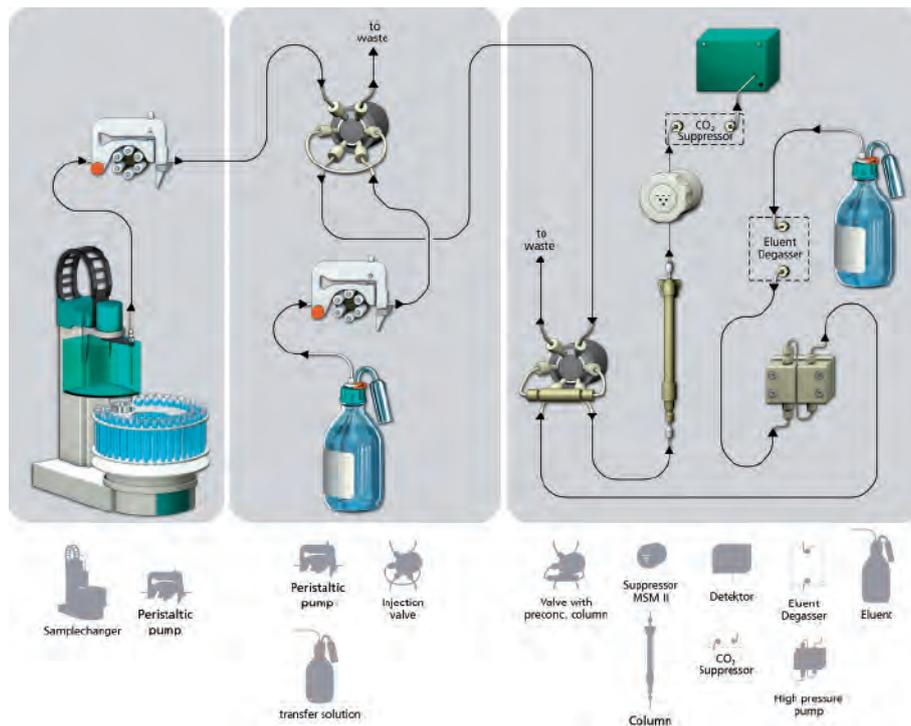
- Halogens and sulfur in liquefied natural gas (LNG) and petroleum gas (LPG)
- Halogens, sulfur, and organic acids in crude oil, gasoline, kerosene, heating oil, and coal (ASTM D 7359)
- Sulfur compounds in amine absorbents (heat stable salts, HSS)
- Amines in various matrices from refineries and petrochemical plants
- Anions, cations, and amines in process and waste water samples and absorption solutions
- Alkali, alkaline earth and transition metals as well as anions in cooling liquids, e.g., monoethyleneglycol «MEG» (ASTM E 2469)
- Anions in emulsions from drilling oils
- Anions and cations in biofuels and fuel blends



Simple matrix elimination

The anions to be determined are freed from the interfering fuel matrix by Metrohm Inline Matrix Elimination. For this purpose, the fuel is injected directly onto a high-capacity preconcentration column. While the anions are retained on the column, the fuel matrix is removed from

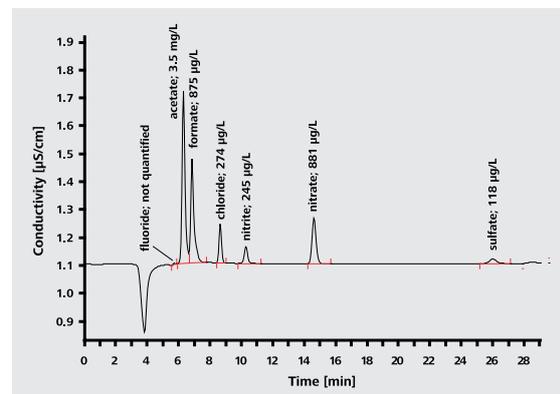
the preconcentration column using a rinsing solution. Then the anions are eluted onto the analytical column. This method allows the additional determination of acetate and formate.



Schematic representation of Metrohm Inline Matrix Elimination



Anion system with Metrohm Inline Matrix Elimination



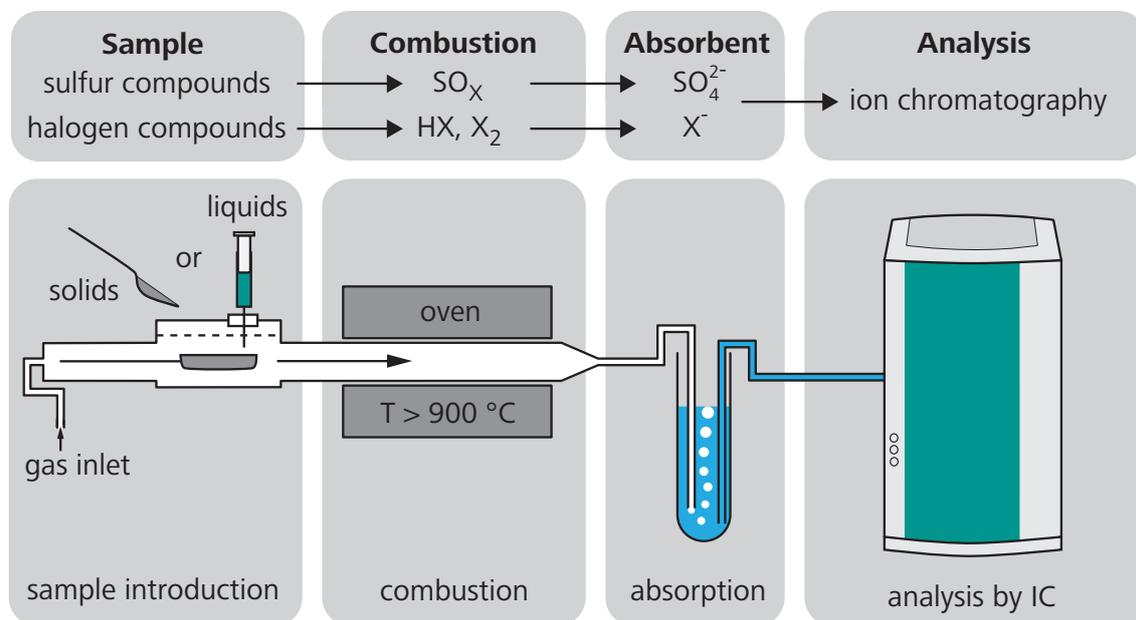
Anions in an E85 gasoline-ethanol blend (85% ethanol, 15% gasoline); column: Metrosep A Supp 7 - 250/4.0 (6.1006.630); Eluent: 3.6 mmol/L Na_2CO_3 , 7.5% acetone, 0.8 mL/min; column temperature 45 °C; sample volume: 10 µL; matrix elimination: transfer solution 7.5% acetone, sample preconcentration with Metrosep A PCC 1 HC/4.0 (6.1006.310)

Halogen and sulfur content: Combustion Ion Chromatography

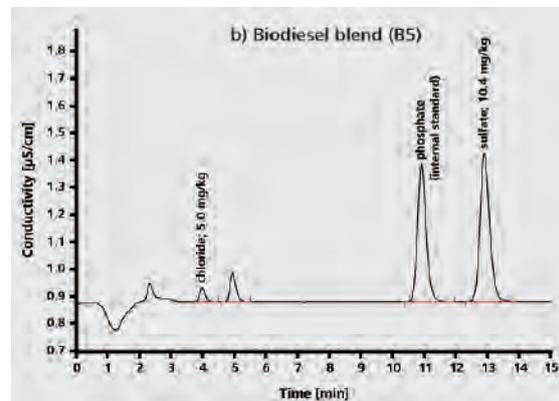
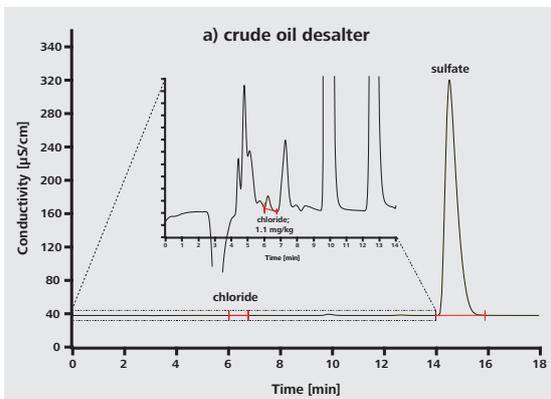
The burning of sulfur-containing fuels leads to the emission of air-polluting sulfur oxides into the atmosphere. Furthermore, high sulfur concentrations have an adverse effect on the ease of ignition of fuels and their stability during storage. Additionally halogen concentrations in the refinery steps from crude oil up to the final product have to be analyzed due to the corrosion risk. A fast and reliable method for determining the halogen and 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, large measuring range and excellent precision and accuracy.

Combustion ion chromatography explained



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 chlorine and sulfur content by Combustion IC in a) crude oil desalter output 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

Voltammetry

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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 a high 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.

797 VA Computrace

The 797 VA Computrace is a modern voltammetric measuring stand that allows voltammetric and polarographic determinations to be carried out. The analyses can also be easily automated by adding Dosinos and a sample changer.





Interesting application examples

Elemental sulfur in gasoline

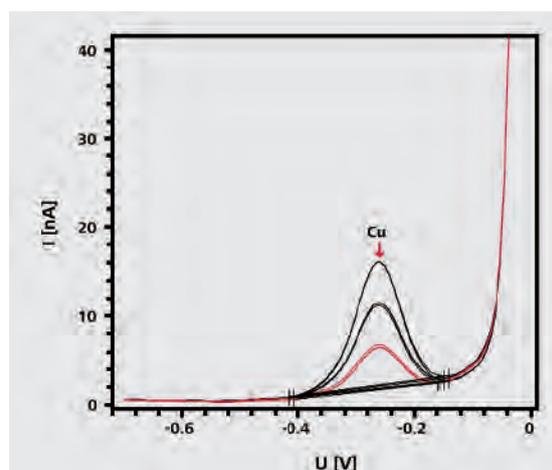
The total sulfur content in petroleum products is normally defined by law and is therefore routinely controlled. It is also of interest to see in which form the sulfur is actually present. By using voltammetry the proportion of elemental sulfur can be determined directly and simply. In this way inferences can be drawn about the influence of gasoline on corrosion processes, for example, regarding sensors in the fuel tank.

Copper in ethanol

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. Using voltammetry, copper can be measured without any sample preparation in pure ethanol or ethanol-gasoline blends (E85, 85% ethanol + 15% gasoline) in the range between 2 $\mu\text{g}/\text{kg}$ and 500 $\mu\text{g}/\text{kg}$.

Heavy metals in petroleum products

The determination of transition metals in petroleum products by voltammetry is usually carried out after digestion. Usually the samples are mineralized or combusted by microwave digestion. Alternatively the metal ions can also be determined after extraction with a mineral acid.



Voltammetric determination of copper

Lab analysis on-line or at-line saves time and money

On-line and at-line Process Analyzers from Metrohm Applikon are the preferred solution for process monitoring in a wide range of industries. Using the complete range of modern ion analysis (titration, KF titration, photometry, ISE standard addition, voltammetry, and direct measurement), Metrohm Applikon Process Analyzers provide high precision results for any wet-chemical parameters you need right at your production line!

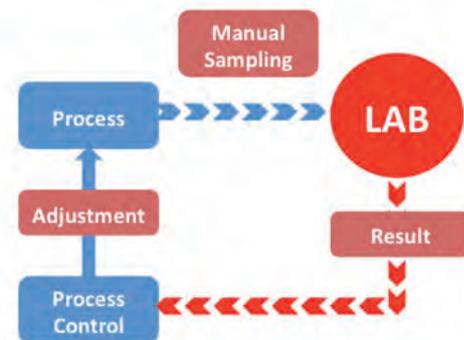
Metrohm Applikon has specialized in on-line and at-line process analysis for over 35 years. With this vast experi-

ence, we offer a wide range of analyzer products and integrated systems for diverse applications and industries to meet the challenging requirements and demands of your process.

Metrohm Applikon is part of the Metrohm Group and represented in over 35 countries. Our regional and local presence offers knowledgeable support in sales, applications, project engineering, and start-up. We intend to be your process monitoring partner for years to come.

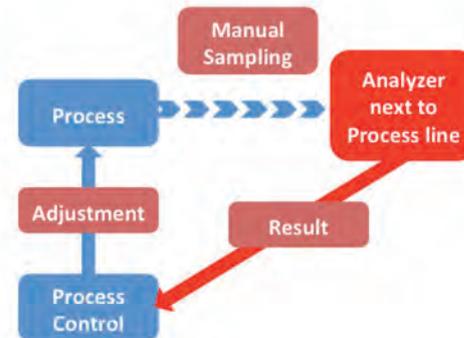
Off-line lab analysis

- Manual sampling
- Sample transport to the lab
- Sample registration



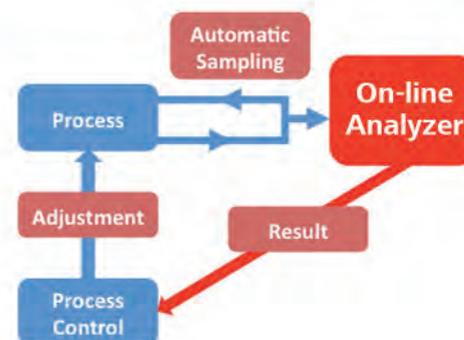
At-line analysis

- Manual sampling
- Continuous manpower needed
- Automated lab analysis close to sampling point inside plant
- Ideal where multiple samples have to be taken at several sampling points along the process



On-line analysis

- In-process measurement & response
- Automated sampling & registration
- Automated sample preconditioning
- Automated lab analysis
- Fast feedback of results
- Very limited manpower needed
- Close loop control



ProcessLab ADI 2045PL – at-line routine analysis in production

The ProcessLab ADI 2045PL is by far the most robust routine system for at-line analysis in everyday use in the plant and control labs. Metrohm Applikon's 35 years experience with on-line analysis has resulted in a new system for custom made at-line process measurements. The

ProcessLab ADI 2045PL guarantees the highest level of reliable analytical results. The new ProcessLab Manager software offers a user-friendly interface in combination with the well proven **tiamo™** lab software.

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Determination of the total acid and total base numbers

The determination of the acid and base numbers is of essential importance for the quality control of petroleum products. The acid number records components that react acidically as a sum parameter and allows conclusions concerning the corrosion of plant or engine components. Over the longer term, petroleum products with high base numbers offer protection from the corrosive influence of any generated acids. By measuring sum parameters, product alterations can be quickly and directly recorded during use.

The determination of acid and base numbers is carried out automatically in the ProcessLab by potentiometric titration in nonaqueous solvents. Because of its proximity to the process, the analytical results are available within minutes.

Production of standard mixtures with a defined octane rating

The octane rating is a measure of a gasoline's resistance to engine knock. In order to assess the octane rating, the resistance to engine knock of a gasoline sample is determined in comparison with standard mixtures showing a predefined octane rating. The standard mixtures, consisting of n-heptane, isooctane (2,2,4-trimethylpentane) and toluene, must be prepared with the highest precision and correctness. ProcessLab is ideal for this thanks to its range of options for liquid handling. The automatic production of dilutions and dilution ranges as well as the doping of additives can be carried out without any further ado. The production of test mixtures is precisely documented and the report can be used as a certificate.

In the same way one can also prepare standard mixtures for measuring cetane numbers with diesel fuels.

On-line process analysis

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In the (petro)chemical industry, continuous control of the production process, the quality of the product and the composition of any waste streams is of utmost importance. With the on-line process analyzers from Metrohm Applikon 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. The Metrohm Applikon analyzers are based on wet-chemical analysis techniques such as titration, photometry, or ion-selective electrode measurements. Analyzers are available for single method, single-stream purposes as well as for complex multiple methods and multiple streams.

In on-line analysis, sampling and sample preconditioning are at least as important as the analyzer itself. Metrohm Applikon has a lot of expertise in this area and is capable of offering custom-made sampling systems, for example, for pressure reduction, filtering, and degassing.

Analysis alone is of no use for process control, and that is why the analyzers 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.

In many cases the IP66-NEMA4 housing of the analyzers will be sufficient. In some cases in the petrochemical industry, however, explosion-proof systems are required. For those circumstances, the ADI 2040 is available in a stainless-steel explosion-proof version for Zone I or Zone II according to the explosive atmosphere directives (ATEX).



On-line Analyzer ADI 2045T

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

Water content

A very important factor in quality control of the petrochemical industry is the determination of the water content in oil. A too high water content has a negative impact on the oil quality. As in the laboratory, Karl Fischer titration (coulometry) is the method of choice for the online determination of the water content in any oil product.



Sampling system for determining the water content in hydrocarbons



Cuvette module for photometric measurements

Salt in crude oil

Excessive amounts of chloride salts in crude oil result in higher corrosion rates in refining units and have a detrimental effect on the catalysts used. Desalting techniques are well established, but continuous control of the salt content is needed for process control and cost reduction. With the ADI 2040 equipped with special heavy duty sample valves, the salt content can be monitored by measuring the conductivity or titration. After each analysis, the measurement vessel is cleaned and a blank measurement is performed before the next sample is taken. For this type of application, the analyzers are configured in an explosion-proof housing.

Hydrogen sulfide and mercaptane determination

Sulfur compounds in oil and oil products cause corrosion and pose an environmental hazard. Determination of H_2S as well as mercaptans is done by titration with silver nitrate, a sulfide-coated silver electrode serving as the indicator electrode.

TBC in styrene

In styrene production, the addition of tertiary-butylcat-echol (TBC) as a stabilizer is critical to prevent the styrene from polymerization during storage and transport. TBC levels need to be maintained above 10...15 mg/L. The problem is that the TBC concentration in styrene will slowly decrease in the presence of oxygen. Using an ADI 2040 with a colorimetric method, TBC levels can be monitored continuously in order to maintain the concentration at the proper level.

 **Metrohm**
Applikon

www.metrohm-applikon.com



Service you can rely on – Metrohm Quality Service

Reliable results for the lifetime of your analytical instruments

From the inspection of the crude oil to the refining process and the quality control of the final products, chemical analysis is in constant demand in the oil industry. Whoever is responsible in the laboratory for the accuracy of the results must not make compromises. Fortunately, systems installed and maintained by professionals on a regular basis all but eliminate the threats of instrument failure and lost profits.

Relying on the Metrohm Quality Service gives you peace of mind from the very start. From the professional installation of your instruments to regular maintenance care and – should a failure ever occur – instant quality repairs, we do everything to make sure that you can rely 100 percent on results produced during the entire lifetime of your Metrohm instruments.

Metrohm Compliance Service

Benefit from the Metrohm Compliance Service when it comes to the professional initial qualification of your analytical instruments. Installation Qualification/Operational Qualification carried out by our experts saves you time and money, as your analytical system is configured according to your needs and put into operation fast and reliably.

Initial instructions and user trainings ensure error-free operation of your new instruments by your staff. The Metrohm Compliance Service includes comprehensive documentation and guarantees compliance with the standards of quality management systems such as GLP/GMP and ISO.

Metrohm Quality Service

Metrohm Quality Service is available worldwide. Preventive maintenance carried out on a regular basis extends your instrument’s lifetime while providing for trouble-free operation. All maintenance work done under the label Metrohm Quality Service is carried out by our own certified service engineers. You can choose the service contract that suits you best.

With a full service contract, for example, you can rely on the optimum performance of your Metrohm instruments, incur no additional costs and benefit from complete and compliant verification documents. Thanks to our service you are perfectly prepared for audits.

An overview of Metrohm Quality Service

Our Services	Benefit for the Customer
Metrohm Care Contracts that, depending on contract type, include preventive maintenance, instrument certification, on-site repair, free or discount on spare parts and consumables as well as guaranteed response times.	Cost certainty and cost savings, coverage of repair risk, quick response times and rapid problem solving, minimal downtimes, and ideal preparation for audits
Application support by means of our vast selection of Application Bulletins, Applications Notes, monographs, validation brochures, technical posters, and articles Personal consultation by our specialists per telephone or e-mail	Quick and professional solution to all arising application questions and complex analytical challenges
Training courses	Competent users contribute substantially to reliable results
Certified calibrations, for example, of dosing and exchange units	Accurate measurements Verification documentation for compliance with regulations and for efficient audits
Remote maintenance Back-up support	Expedient resolution of software questions High data security
Emergency service, for example, express on-site repairs	Short response times and thus, rapid problem resolution Minimization of downtime
Original spare parts, made in Switzerland and available world wide Guaranteed spare parts available for at least 10 years beyond instrument discontinuation date	Lasting, successful repair; short delivery times Minimization of downtime Protection of your investment through long-term availability of spare parts and accessories
Decentralized repair workshops located around the world and a central workshop in Switzerland	Quality repairs done quickly, so your instruments are ready for use again



Ordering information

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Titration

2.848.3010	Oil Titrino plus
2.905.3010	Oil Titrando
2.855.2010	Robotic TAN/TBN Analyzer
2.864.1130	Robotic Balance Sample Processor TAN/TBN
6.0229.010	Solvotrode easyClean, 1 m cable
6.0229.020	Solvotrode easyClean, 2 m cable
6.0430.100S	Ag-Titrode with Ag ₂ S coating
6.1115.000	Optrode
6.6040.00X	Application collection «Oil PAC»

Water determination according to Karl Fischer

Coulometric KF titration

2.831.0010	831 KF Coulometer including generator electrode with diaphragm and 728 Magnetic Stirrer
2.831.0110*	831 KF Coulometer including generator electrode without diaphragm
2.756.0010	756 KF Coulometer with built-in printer including generator electrode with diaphragm and 728 Stirrer (magnetic stirrer)
2.756.0110*	756 KF Coulometer with built-in printer including generator electrode without diaphragm
2.851.0010	851 Titrando including generator electrode with diaphragm and 801 Magnetic Stirrer
2.851.0110*	851 Titrando including generator electrode without diaphragm
2.852.0050	852 Titrando including generator electrode with diaphragm and 801 Magnetic Stirrer
2.852.0150*	852 Titrando including generator electrode without diaphragm
2.899.0010	899 Coulometer with built-in stirrer including generator electrode with diaphragm
2.899.0110	899 Coulometer with built-in stirrer including generator electrode without diaphragm

* The Magnetic Stirrer has to be ordered separately.

Volumetric KF titration

2.870.0010	870 KF Titrino plus
2.890.0110	890 Titrando with Touch Control
2.901.0010	901 Titrando including titration cell and indicator electrode
2.915.0110	915 Ti-Touch with built-in stirrer
2.916.3010	Oil Ti-Touch

KF Oven

2.860.0010	860 KF Thermoprep
2.874.0010	874 Oven Sample Processor
2.885.0010	885 Compact Oven Sample Changer
2.136.0200	KF Evaporator

Voltammetry

2.797.0010	797 VA Computrace for manual operation
MVA-2	VA Computrace system with automatic standard addition. Consisting of 797 VA Computrace with two 800 Dosinos.
MVA-3	Fully automated VA Computrace system. Consisting of 797 VA Computrace with 863 Compact VA Autosampler and two 800 Dosinos for automatic addition of auxiliary solutions. Allows the automatic processing of up to 18 samples. This system is the optimal solution for the automatic analysis of small sample series.

Oxidation stability

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

Ion chromatography**Anions and cations in «Produced water»**

2.881.0030	881 Compact IC pro – Anion – MCS
2.881.0010	881 Compact IC pro – Cation
2.850.0910	2 x 850 Conductivity IC Detector
2.858.0020	858 Professional Sample Processor – Pump
6.2041.440	Sample Rack 148 x 11 mL
6.1006.430	Metrosep A Supp 4 - 250/4.0
6.1007.000	Nucleosil 5SA
6.6059.242	MagIC Net™ 2.4 Professional

Options

6.5330.000	Dialysis equipment
2.858.0030	858 Professional Sample Processor – Pump – Injector
2.800.0010	800 Dosino
6.3032.120	Dosing Unit 2 mL
6.2841.100	Washing station for IC Sample Processor

Anions in gasoline-ethanol blends

2.850.2150	850 Professional IC Anion – MCS – Prep 2
2.850.9010	850 Conductivity IC Detector
2.858.0010	858 Professional Sample Processor
6.2041.390	Sample Rack 16 x 120 mL
6.1006.630	Metrosep A Supp 7 - 250/4.0
6.1006.310	Metrosep A PCC 1 HC
6.1014.200	Metrosep I Trap column
6.6059.242	MagIC Net™ 2.4 Professional

Options

2.800.0010	800 Dosino
6.3032.210	Dosing Unit 10 mL
6.2841.100	Washing station for IC Sample Processor

Combustion IC

2.881.3030	Metrohm Combustion IC
6.1006.520	Metrosep A Supp 5 - 150/4.0

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