Safety First

Chemical Analytics for Defense & Security

**PEOPLE
YOU
CAN
TRUST**

Metrohm

1. Table of contents

2. Safety First

Precision analytics for defense & security
The need for chemical analytics is omnipresent in defense & security. The safe operation of vehicles, aircraft and ships must always be ensured and thus operational capability guaranteed. If the parameters are right and analytical norms and standards are met, an important step has already been taken towards fulfilling the order.

The same applies to the safety of soldiers. Here, too, analytics makes an important contribution to health and safety.

The focus below is therefore on presenting analytical procedures that ensure safe use. With “Safe Operations”, the focus is not only on technology but especially on the troops as an integral part of the system.

Corrosion addresses a key area that is responsible for high running costs and is relevant to safety. The **quality control of hydraulic oils, coolants, lubricants, and fuels** is essential for safe operations and contributes to the flawless and long-term functioning of technical systems. Analysis of **breathing air** is an integral niche application. In contrast, **water analytics** is of vital importance in many areas: Poor drinking water quality is devastating to soldiers. Water quality is also of paramount importance in the areas of drives and power plants. The fact that wet powder does not fire is a banality. Especially when **propellant and explosive charges** are stored for a long time, regular examination of their condition and quality is absolutely essential. In addition to quality control, the qualitative verification of **explosives** plays a major role in the removal of explosives and forensics. Another safety-relevant area is the qualitative and quantitative analysis of **chemical warfare agents**. In addition, analytics ensure that only tested **pharmaceuticals** are used. Metrohm analytical instruments make an important contribution here as well.

METROHM – PEOPLE YOU CAN TRUST

Corrosion is dangerous and gives rise to very high costs.

3. Corrosion

Corrosion is a process of wear and tear that attacks metals and their alloys and degrades over time. The visible effect is the formation of rust. Metrohm offers armed forces extensive know-how and technical solutions for corrosion measurement, prevention, and protection. The main focus here is on monitoring electroplating baths. Furthermore, the underlying processes of corrosion can also be measured directly, providing information about the causes.

Most corrosion phenomena are electrochemical in nature and consist of at least two reactions on the surface of the corroding metal. One of the reactions is oxidation (e.g., disintegration of iron), also referred to as anodic partial reaction. The other is a reduction reaction (e.g., reduction of oxygen) and is referred to as a cathodic partial reaction. The products of the electrochemical reactions can react non-electrochemically with each other and form the final product (e.g., rust).

Documentation	**WP-044** “Principles of electrochemical corrosion research” **AN-COR-001** “Corrosion Part 1 – Basic terms” **AN-COR-002** “Corrosion Part 2 – Calculation of corrosion parameters with NOVA” **AN-COR-003** “Corrosion Part 3 – Measurement of polarization resistance” **AN-COR-004** “Corrosion Part 4 – Equivalent electrical circuits” **AN-COR-005** “Corrosion Part 5 – Corrosion inhibitors”

3.1 Measuring corrosion

Changes in the electrochemical conditions of metallic surfaces reveal corrosion processes that take place covertly. These processes must be measured and prevented before they become critical.

3.1.1 CORROSION MEASUREMENTS ON METALS

3.1.1.1 Corrosion measurements on metals and metallic surfaces

Application	Corrosion measurements on different metals
Technology	Electrochemical impedance spectroscopy Potentiodynamic polarization
Documentation	**AN-COR-010** "Electrochemical corrosion studies on different metals"

The change in metallic surfaces can be measured with Metrohm devices.

3.1.2 CORROSION MEASUREMENTS IN BUILDING MATERIALS

3.1.2.1 Corrosion measurements of solid substances

Application	Determination of fluorine and chlorine
Technology	Ion chromatography for anions with chemical suppression after combustion (combustion ion chromatography)
Documentation	**Brochure 8.000.5248** "Fast and reliable determination of halides and sulfur by pyrohydrolysis"

As different as the many types of cement may be, what characterizes all of them equally is the presence of the elements calcium, magnesium, iron, aluminum, and silicium.

Application	Determination of aluminum in cement
Technology	Photometric titration with the Optrode
Documentation	**AB-063** "Silicium, calcium, magnesium, iron and aluminum in cement after digestion and photometric titration" **AN-T-078** "Determination of aluminum in cement by photometric titration"
Standards	EN 196-2, ISO 29581-1
Application	**Determination of iron in cement**
Technology	Potentiometric titration with the Ag Titrode
Documentation	**AN-T-006** "Chloride traces in cement and clinker brick"
Standards	ISO 29581-1
Application	**Determination of iron in cement**
Technology	Photometric titration with the Optrode
Documentation	**AB-063** "Silicium, calcium, magnesium, iron and aluminum in cement after digestion and photometric titration" **AN-T-080** "Determination of iron in cement by photometric titration"
Standards	EN 196-2, ISO 29581-1
Application	**Determination of calcium in cement**
Technology	Photometric titration with the Optrode
Documentation	**AB-063** "Silicium, calcium, magnesium, iron and aluminum in cement after digestion and photometric titration" **AN-T-079** "Determination of calcium in cement by photometric titration of the dissolved product in accordance with EN 196–2"
Standards	EN 196-2, ISO 29581-1

Application	Determination of magnesium in cement
Technology	Photometric titration with the Optrode
Documentation	**AB-063** "Silicium, calcium, magnesium, iron and aluminum in cement after digestion and photometric titration" **AN-T-081** "Determination of magnesium in cement by photometric titration"
Standards	EN 196-2, ISO 29581-1

3.1.3 CORROSION MEASUREMENTS IN COOLING WATER

3.1.3.1 Boiler feed water

Corrosion is the natural enemy of steam power plants and propulsion systems. It affects pipes, turbine blades, valves, and rotors of plants regardless of whether the systems in question are operated with conventional or nuclear fuel. Corrosion is particularly crucial in supercritical power plants, as the corrosion processes are extremly aggressive due to the lack of phase transitions.

The protection of the plants, which at the same time ensures safe operation, is of paramount importance for land-based systems. At sea, it is essential for survival.

Application	Determination of anions in boiler feed water (traces and ultra-traces)
Technology	Ion chromatography for anions with chemical suppression
Documentation	**AN-S-206** "Online monitoring of trace anions in boiler feed water"

The iron concentration in the boiler feed water must be monitored to ensure reliable and safe operation of the water-steam circuit. Different guidelines set limits for the maximum iron content.

Application	Determination of iron in boiler feed water
Technology	Adsorptive stripping voltammetry (AdSV)
Documentation	**AN-V-179** "Iron in boiler feed water – Uncomplicated, sensitive and cost-effective determination by adsorptive stripping voltammetry (DHN Method)"

3.2 Preventing corrosion

3.2.1 CORROSION CONTROL IN FUELS

Impurities in fuels (gasoline, kerosene, crude oil, heating oil, coal, butane, propane, natural gas, etc.) caused by halides and sulfur compounds promote corrosion of metallic surfaces in pipelines, tanks, valves, and engines. Accurate monitoring is therefore essential.

3.2.1.1 Determination of halides and sulfur in fuels

Application	**Determination of fluoride, chloride, bromide, and sulfate in Fuels**
Technology	Ion chromatography for anions using combustion ion chromatography
Documentation	**Brochure 8.000.5248** "Combustion ion chromatography – Fast and reliable determination of halides and sulfur by pyrohydrolysis"
Standards	ASTM D7359, UOP991, ASTM D5987, ASTM D7994

High temperature combustion is used to measure corrosion indicators.

3.2.2 CORROSION MEASUREMENTS IN BOILER FEEDWATER AND COOLING WATER

During the operation of turbines of conventional and nuclear ship drives, corrosion can be slowed down or completely prevented by the alkaline provision of the cooling water and feed water or the addition of inhibitors (e.g., phosphates and amines). The measurement of corrosion inhibitors therefore also ensures the safe and long-term operation of the systems.

3.2.2.1 Measurement of corrosion indicators and inhibitors in boiler feed water

Boiler feed water is the operating medium in thermal power plants. To suppress corrosion, the pH of the feed water is adjusted with amines. Their addition must be regularly monitored. In addition, monitoring sodium concentration is critical, as an increase is likely to indicate penetration of cooling water due to a condenser leak. Ion chromatography with conductivity detection after sequential suppression is a powerful monitoring tool, especially in combination with intelligent preconcentration technology and matrix elimination.

Application	**Determination of lithium and sodium in addition to monoethanolamine in the water-steam circuit of thermal power plants**
Technology	Ion chromatography for cations
Documentation	**AN-CS-010** "Traces of lithium and sodium in addition to monoethanolamine in water-steam circuits of power plants"

3.2.2.2 Corrosion inhibitors in cooling water and coolants

In industrial cooling water systems and ship cooling systems, copper and copper alloys are usually used, since they conduct heat extremely well. However, these materials are sensitive to corrosion. Azoles serve as corrosion protection for copper and its alloys. Their determination is performed by ion chromatography and UV/VIS detection.

Application	**Determination of corrosion inhibitors (benzotriazole, tolytriazole, mercapto-benzotriazole) in cooling water**
Technology	Ion chromatography for cations with UV/Vis detection
Documentation	**AN-U-060** "Corrosion inhibitors in cooling water"

3.2.2.3 Determination of pH

Corrosion of metallic components is an inherent problem for engines, since metals naturally tend to oxidize in the presence of water and/or acids. Increased acidity is indicated by low pH and can lead to a variety of problems, such as a shorter storage stability or a reduced buffer capacity of the engine coolant or rust inhibitor used.

Application	**pH of engine coolants or rust inhibitors – Rapid determination in accordance with ASTM D1287**
Technology	pH measurement, direct measurement with Profitrode
Documentation	**AN-T-201** "pH of engine coolants or rust inhibitors – Rapid determination in accordance with ASTM D1287"
Standards	ASTM D1287

Monitoring the pH in the primary and secondary cooling water circuit of nuclear vessels provides information on the service life of corrosion inhibitors.

Application	**Determination of pH in cooling water**
Technology	pH measurement, direct measurement with Aquatrode plus
Documentation	**AN-T-076** "Conductivity, pH, alkalinity, hardness and chloride content of tap water – Fully automated determination including sample preparation" **AN-T-205** "Fully automated water analysis with OMNIS" **AB-188** "pH measurement technology"
Standards	ASTM D1293, ASTM D5464, EN ISO 10523, EPA 150.1

3.3 Protection against corrosion

Metallic surfaces (e.g., steel) can be effectively protected against corrosion by electrochemical coating processes (electroplating) or protective coatings. This increases the service life of the components and increases operational safety.

3.3.1 MONITORING PROTECTIVE COATINGS

In the past, zinc chromate pigment was frequently used in the aerospace industry for its rust-protecting and corrosion-inhibiting properties.

As an additive in paint primers for steel and aluminum surfaces, it proved to be particularly effective in preserving the structural integrity of military vehicles as well as commercial and private aircraft. However, the longstanding concern about the health risks associated with exposure to zinc chromate led to strict regulations in the 1970s and subsequently to a gradual phase-out of the use of zinc chromate products in commercial and industrial applications. Because of this, there is a need for robust forensic technologies for the rapid and accurate identification of zinc chromate and other hexavalent chromium compounds in complex test samples. Handheld Raman spectroscopy is a well-known technique that meets the criteria for fast and flexible identification of materials. A drawback might be that the target signal from 785 nm systems can be disturbed by fluorescence, which is particularly problematic with mixtures, dyes, and materials. The solution to this challenge is the MIRA XTR DS Raman analyzer, which uses fluorescence suppression to ensure safe, precise results when analyzing potentially chromium-containing colors.

Protective coatings preserve metallic surfaces

3.3.1.1 Determination of primers

Application	Mobile detection of chromium (VI) in protective coatings in various chromates (Ag, Ba, Ca, Na, Zn)
Technology	Raman spectroscopy with MIRA DS XTR @ 785 nm
Documentation	**Whitepaper WP-073** "On-site determination of hexavalent chromium in protective primers"

3.3.2 MONITORING OF ELECTROPLATING BATHS

3.3.2.1 Electroplating baths (general)

Application	Determination of fluoride, lactate, acetate, amidosulfonate, nitrite, nitrate, sulfate, tartrate, oxalate, and citrate in electroplating baths
Technology	Ion chromatography for anions with chemical suppression
Documentation	**AN-S-165** "Hypophosphite, phosphite, tartrate, tungstate, phosphate, citrate, and pyrophosphate in an electroplating bath" **AN-S-166** "Hypophosphite, phosphite, tartrate, tungstate, phosphate, citrate, and pyrophosphate in the presence of standard anions"

3.3.2.2 Monitoring anodizing electroplating baths

Application	Determination of aluminum (total metal) in anodizing baths
Technology	Potentiometric titration with the Profitrode (acid-base titration)
Documentation	**AB-089** "Potentiometric analysis of anodizing baths"
Application	**Determination of chloride in anodizing baths**
Technology	Potentiometric titration with Ag Titrode (precipitation titration)
Documentation	**AB-130** "Potentiometrically indicated chloride titrations" **AB-089** "Potentiometric analysis of anodizing baths"
Application	**Determination of chromic acid in anodizing baths**
Technology	Potentiometric titration with the Pt Titrode (redox titration)
Documentation	**AB-089** "Potentiometric analysis of anodizing baths"
Application	**Determination of oxalic acid in anodizing baths**
Technology	Potentiometric titration with Pt Titrode (redox titration)
Documentation	**AB-089** "Potentiometric analysis of anodizing baths"
Application	**Determination of sulphuric acid inanodizing baths**
Technology	Potentiometric titration with the Profitrode (acid-base titration)
Documentation	**AB-089** "Potentiometric analysis of anodizing baths"
Application	**Determination of sulphuric acid and tartaric acid in anodizing baths**
Technology	Thermometric titration
Documentation	**AN-H-143** "Sulphuric acid and tartaric acid in tartaric acid-sulphuric acid anodizing baths – Fast, sequential determination with a thermometric sensor (thermometric titration)"

3.3.2.3 Monitoring of etching baths

Application	Determination of anions in etching baths
Technology	Ion chromatography for anions with chemical suppression and conductivity and UV detection
Documentation	**AN-S-284** "Anions in etching baths"
Application	**Automated determination of mixtures of HNO3, HF and H2SiF6 in the range of approx. 200–600 g/L HNO3, 50–160 g/L HF and 0–185 g/L H2SiF6 in etching acid mixtures**
Technology	Thermometric titration
Documentation	**AB-344** "Automated analysis of etching fluid mixtures with the 859 Titrotherm and the 814 USB Sample Processor"

3.3.2.4 Monitoring lead baths

Application	Lead determination
Technology	Potentiometric titration with the copper ISE and the Profitrode
Documentation	**AB–092** "Potentiometric analysis of lead baths"

3.3.2.5 Monitoring bronze baths

Application	Determination of copper, tin and free cyanide
Technology	Potentiometric titration with copper ISE and Ag Titrode
Documentation	**AB–091** "Potentiometric analysis of brass and bronzing baths"

3.3.2.6 Monitoring chrome baths

Application	Determination of Cr(VI) and Cr(III) in chrome baths
Technology	Potentiometric titration with Pt Titrode (redox titration)
Documentation	**AN-T-020** "Cr(VI) and Cr(III) in chrome baths"

Application	Determination of sulfate and catalysts in chrome baths
Technology	Anion chromatography with chemical suppression and conductivity detection
Documentation	**AN-S-328** "Sulfate in addition to chromate in bright chrome baths"

3.3.2.7 Monitoring of cadmium baths

Application	Determination of H^+ or OH^- in cadmium baths
Technology	Potentiometric titration with the Profitrode (acid-base titration)
Documentation	**AB-093** "Potentiometric analysis of cadmium baths"
Application	**Determination of free cyanide in cadmium baths**
Technology	Potentiometric titration with Ag Titrode (precipitation titration)
Documentation	**AB-046** "Potentiometric cyanide determination" **AB-093** "Potentiometric analysis of cadmium baths"

Constant online monitoring of electroplating baths ensures reliable results

Application	Determination of cadmium in cadmium baths
Technology	Potentiometric titration with Cu ISE (Ag/AgCl reference) (complexometric titration)
Documentation	**AB-101** "Complexometric titrations with Cu ISE" **AB-093** "Potentiometric analysis of cadmium baths"

3.3.2.8 Monitoring copper and brine baths

Application	Determination of H^+ or OH^- in copper and brine baths
Technology	Potentiometric titration with the Profitrode (acid-base titration)
Documentation	**AN-T-023** "Hydroxide and carbonate in alkali electroplating baths for cadmium, copper, lead or zinc"
Application	**Determination of free cyanide in copper baths**
Technology	Potentiometric titration with Ag Titrode (precipitation titration)
Documentation	**AB-046** "Potentiometric cyanide determination"

Application	Determination of copper in copper baths
Technology	Potentiometric titration with Cu ISE (Ag/AgCl reference) (complexometric titration)
Documentation	**AB-101** "Complexometric titrations with Cu ISE"

3.3.2.9 Monitoring brass baths

Application	Determination of zinc, free cyanide, ammonium, carbonate, sulfite in brass baths
Technology	Potentiometric titration with copper ISE and Ag Titrode
Documentation	**AB-091** "Potentiometric analysis of brass and bronzing baths"

3.3.2.10 Monitoring nickel baths

Application	Determination of antimony in electroless nickel baths
Technology	Anodic Stripping Voltammetry (ASV)
Documentation	**AN-V-151** "Antimony (III) and antimony (total) in a electroless nickel bath"

Electroplating protects against corrosion and thus ensures safe operation – here, of an airplane nose landing gear

Application	Determination of boric acid in nickel baths
Technology	Potentiometric titration with the Profitrode (acid-base titration)
Documentation	**AB-195** "Titrimetric determination of free boric acid and tetrafluoroboric acid in nickel baths"
Application	**Determination of chloride in nickel baths**
Technology	Potentiometric titration with Ag Titrode (precipitation titration)
Documentation	**AB-130** "Potentiometrically indicated chloride titrations"
Application	**Determination of hypophosphite, phosphite and phosphate in nickel baths**
Technology	Anion chromatography with chemical suppression and conductivity detection
Documentation	**AN-S-247** "Hypophosphite, phosphite and phosphate in a nickel plating bath"
Application	**Determination of nickel in nickel baths**
Technology	Potentiometric titration with Cu ISE (Ag/AgCl reference) (complexometric titration)
Documentation	**AB-101** (general titrations with Cu ISE)
Application	**Determination of fluoride, chloride and nitrate in nickel baths**
Technology	Anion chromatography with chemical suppression and conductivity detection
Documentation	**AN-S-024** "Fluoride, chloride and nitrate in an acidic nickel/zinc bath"
Application	**Determination of phosphoric acid in nickel baths**
Technology	Potentiometric titration with Pt Titrode (redox titration)
Documentation	**AN-N-063** "Nitrate in a nickel plating bath"

3.3.2.11 Monitoring phosphating baths

Application	Acid content in phosphating baths
Technology	Potentiometric titration with the Profitrode (acid-base titration)
Documentation	**AB-289** "Monitoring parameters in a phosphating process (pH, conductivity, acidity, alkalinity, fluoride and zinc)"

3.3.2.12 Monitoring cleaning baths

Application	Determination of H^+ or OH^- in cleaning baths
Technology	Near Infrared Spectroscopy (NIRS) with the XDS Process Analyzer
Documentation	**AN-PAN-1055** "Monitoring of quality parameters in standard cleaning baths – Simultaneous measurement of ammonium hydroxide, hydrogen peroxide and hydrochloric acid using inline analysis"

3.3.2.13 Monitoring silver baths

Application	Determination of free cyanide in silver baths
Technology	Potentiometric titration with Ag Titrode (precipitation titration)
Documentation	**AB-046** "Potentiometric cyanide determination"
Application	**Determination of silver in silver baths**
Technology	Potentiometric titration with Ag Titrode (precipitation titration)
Documentation	**AB-046** "Potentiometric cyanide determination", **AB-061** "Potentiometric determination of silver – Accurate determination in accordance with the standards EN ISO and GB/T"
Standards	EN ISO 11427, ISO 13756, GB/T 17823, GB/T 18996

3.3.2.14 Monitoring of brine baths

Application	Determination of chloride in brine baths
Technology	Potentiometric titration with Ag Titrode (precipitation titration)
Documentation	**AB-130** "Potentiometrically indicated chloride titrations"

3.3.2.15 Monitoring zinc baths

Application	Determination of zinc in zinc baths
Technology	Potentiometric titration with Cu ISE (Ag/AgCl reference) (complexometric titration)
Documentation	**AB-101** "Complexometric titrations with Cu ISE"
Application	**Determination of fluoride, chloride and nitrate in zinc baths**
Technology	Anion chromatography with chemical suppression and conductivity detection
Documentation	**AN-S-024** "Fluoride, chloride and nitrate in an acidic nickel/zinc bath"

3.3.2.16 Monitoring tin baths

Application	Determination of tin(II), tin(IV) and total tin
Technology	Potentiometric titration with the Pt Titrode
Documentation	**AB-090** "Potentiometric analysis of tin baths"

The hydraulics must function perfectly every second. The quality of the hydraulic oils used is essential for this.

4. Quality control of hydraulic oils, coolants, lubricants, and fuels

Fuels such as aircraft fuel, diesel, and gasoline must be of the highest quality. In addition, they cannot be stored indefinitely since they are subject to aging. The same applies to high performance lubricants and oils. Similarly demanding is quality control, during which numerous parameters need to be determined. Metrohm offers the most up-to-date measuring instruments for the analysis of fuels and lubricants, all of which deliver precise and reproducible measurement results.

4.1 Quality determination in hydraulic oils

Hydraulic oils are essential for controlling and operating vehicles, aircraft, helicopters, and ships. Although these oils are mostly used in closed systems, they are in contact with the ambient air and are therefore exposed to oxidation processes. The partially hygroscopic substances store water. This can lead to ice formation when used below 0° Celsius and thus become an acute risk. In addition, hydraulic oils are subjected to thermal loads that cause them to age and reduce their functionality. Quality controls and periodic checks are therefore essential.

4.1.1 Determination of the base number in hydraulic oils

(Also used for lubricants and fuels)

As hydraulic oils age, acids form that can lead to massive corrosion. For this reason, alkaline additives are added to the hydraulic oils by the manufacturers. The (remaining) base number is determined as an indicator.

Alkaline chemicals are added to hydraulic oils to prevent corrosion, since they neutralize acidic components that form during the use and aging of these products. The base number (BN) gives an indication of the amount of these alkaline additives and can be used as a measure of the degradation of the respective hydraulic oil.

In the literature, the designation TBN = Total Base Number is often used. This term has now been replaced by the abbreviation BN = Base Number.

Anwendung	Determination of the base number (BN) in hydraulic oils
Application	Determination of the base number
Technology	a) Potentiometric titration with Solvotrode easyClean b) Photometric titration with the Optrode c) Thermometric titration with the Thermoprobe
Documentation	a, b, c) **AB-405** "Determination of total base number in petroleum products" a) **AN-T-179** "Determination of the acid number of fresh engine oil in accordance with ASTM D664 and IP 177 as well as the base number in accordance with ISO 3771" b) **AN-T-093** "Total base number in used engine oil" c) **AN-H-096** "Determination of the total base number of lubricating oils"
Standards	ASTM D2896, ISO 3771 IP 276 (Potentiometric titration) ASTM D974 ISO 6618 (Photometric titration) ASTM under discussion (Thermometric titration) IP 400 (Conductometric titration)

4.1.2 Determination of the acid number in hydraulic oils

(Also used for lubricants and fuels)

Determination of the acid number is an important parameter in the quality control of "POL" (Petrol, Oil, Lubricants). This parameter must be determined periodically in order to ensure the operational safety of vehicles, aircraft and ships.

During the use of hydraulically operated equipment, the hydraulic oil comes into contact with atmospheric oxygen. This leads to oxidation and acid formation. High temperatures and metals as catalysts accelerate this process. The amount of acid "AN" determines the quality of the hydraulic oil and can be used as an indicator for a possible oil change.

Fresh and used hydraulic oils can contain acidic components as additives or degradation products. The acid number (AN) is a measure of the relative amount of acids present, expressed as mg KOH per gram of sample. In addition, the AN is used as a quality parameter of lubricating oils both to assess the quality of new formulations and as an indicator of the degradation of these formulations during operation.

The determination of the acid number plays an important role in the analysis of petroleum products. This is reflected in the numerous standard procedures used worldwide (internal specifications of multinational companies, national and international specifications of ASTM, DIN, IP, ISO, etc.). These procedures differ mainly in the composition of the solvents and titrants used.

In the literature, the designation TAN = Total Acid Number is often still used. This term has now been replaced by the abbreviation AN = Acid Number.

The procedures described mainly differ in the composition of the solvents and titrants used.

Application	Determination of the acid number (AN = Acid Number)
Technology	a) Potentiometric titration with Solvotrode easyClean b) Photometric titration with the Optrode c) Thermometric titration with the Thermoprobe
Documentation	a, b, c) **AB-404** "Determination of total acid number in petroleum products" a) **AN-T-096** "Acid number of lubricating and engine oil – Reliable determination in accordance with ASTM D664 and IP 177" a) **AN-T-179** "Determination of the acid number of fresh engine oil in accordance with ASTM D664 and IP 177 as well as the base number in accordance with ISO 3771" b) **AN-T-092** "Acid number of isolation, transformer and turbine oils – Using a photometric sensor increases precision and reliability for determination in accordance with ASTM D974" c) **WP-012** «Avoiding corrosion: A new method for TAN determination in crude oil and petroleum products" c) **WP-013** "Acid number in crude oil and petroleum products" c) **AB-427** "Acid number in crude oils and petroleum products by thermometric titration in accordance with ASTM D8045"
Standards	a) ASTM D664, IP 177 (Potentiometric titration) b) ASTM D974 (Photometric titration) c) ASTM D8045 – Thermometric titration – is much faster compared to ASTM D664, requires fewer reagents and only minimal sensor maintenance, which makes it much more cost-effective.

4.1.3 Determination of water content in hydraulic oils

(Also used for lubricants and fuels)

Water in crude, insulating, lubricating and turbine oil can cause corrosion, which in turn leads to an increased load of dirt and thus to reduced lubrication and clogged filters. As a result, high water content can lead to damage to infrastructure, higher maintenance costs or even undesirable downtimes.

Due to the factors mentioned above, water content is an important factor that is regulated in many trade specifications and also determines the price of these substances. Accurate and reliable determination is therefore necessary, as even small deviations can have a great influence on quality and price.

Application	Determination of water content by Karl Fischer titration
Technology	Karl Fischer titration (volumetric and coulometric)
Documentation	a) **AB-209** "Water in insulating oil, hydrocarbons and their products – Precise and reliable determination by Karl Fischer titration" b) **AB-137** "Coulometric Karl Fischer water content determination" c) **AN-K-070** "Water in petroleum products – Fully automated determination in accordance with ASTM D6304", **WP-061** "Water content in petroleum products in accordance with ASTM D6304"
Standards	a) ASTM D6304, ASTM E1064, ASTM D1533, ASTM D3401, ASTM D4928, EN IEC 60814, EN ISO 12937, ISO 10337, DIN 51777 and GB/T 11146. The drying oven method is described in accordance with ASTM D6304, EN IEC 60814 and DIN 51777 b) ASTM E1064 c) ASTM D6304

4.2 Quality determination in coolants and rust inhibitors

4.2.1 Determination of pH in engine coolants and rust inhibitors

Corrosion on metallic components is an inherent problem for engines, as metals naturally tend to oxidize in the presence of water and/or acids. Increased acidity is indicated by a low pH and can lead to a variety of problems, such as such as a shorter storage stability or a reduced buffer capacity of the engine coolant or rust inhibitor used. This in turn leads for example to a shortened service life for engines. Without proper coolants and rust inhibitors, engines can overheat and seize up, which may result in costly damage and additional maintenance or even complete replacement of the affected parts.

Application	Determination of pH
Technology	pH Measurement with the Profitrode
Documentation	**AN-T-201** "pH of engine coolants or rust inhibitors – Rapid determination in accordance with ASTM D1287"
Standards	ASTM D1287 (coolants, anti-rust agents) ASTM D8086 (non-aqueous coolants) ASTM D3306, D7713, E1177 (glycol-based coolants for vehicles) ASTM D7388, D7518 (1.3-propanediol (PDO) based coolants) ASTM D4985, D5752 (coolants for high performance engines) ASTM D7640, D7714 (glycerine-based coolants)

4.2.2 Determination of reserve alkalinity in coolants

The reserve alkalinity of engine coolants and rust inhibitors is an indicator of the buffering capacity or capacity to absorb acids. These acids can be introduced, for example, through exhaust gas leaks, residues of acidic cleaners or oxidation of ethylene glycol or propylene glycol.

Reserve alkalinity is often used for quality control during production and often listed in coolant specifications. Fast and accurate determination is therefore important.

The use of the fully automated Metrohm OMNIS titration system for this routine analysis enables a more accurate and reliable determination because automation reduces the risk of human error. In addition, the operator is free to perform other tasks, increasing the efficiency of the lab.

Application	Determination of reserve alkalinity in quality control
Documentation	**AN-T-202** "Reserve Alkalinity of engine coolants – Uncomplicated determination in accordance with ASTM D1121"
Technology	Potentiometric titration with the Profitrode
Standards	ASTM D1121 (coolants, anti-rust agents) ASTM D8085 (non-aqueous coolants) ASTM D3306 (glycol-based coolants for vehicles) ASTM D7518 (1.3-propanediol (PDO) based coolants) ASTM D4985, D5752 (coolants for high performance engines) ASTM D7714 (glycerine-based coolants)

4.2.3 Determination of water content in coolants and lubricants

Anwendung	Determination of water content in coolants and lubricants
Application	Determination of water content in non-aqueous coolants for quality control
Documentation	a) **AB-077** "Volumetric Karl Fischer water content determination – Tips and tricks for volumetric Karl Fischer titration" b) **AB-137** "Coulometric Karl Fischer water content determination"
Technology	Volumetric or coulometric Karl Fischer titration
Standards	a) ASTM E203 b) ASTM E1064

4.2.4 Determination of chloride content (traces) in coolants

Application	Determination of chloride content (traces)
Technology	Potentiometric titration with the Ag Titrode
Documentation	**AB-130** "Potentiometrically indicated chloride titrations" (ASTM D3634)
Standards	ASTM D3634

4.2.5 Determination of halides and other anions in coolants

Application	Determination of halides in coolants
Documentation	**AN-S-219** «"Anions and organic acids in engine coolants" **AN-S-285** "Anions in cooling lubricant after Metrohm inline dialysis"
Technology	Ion chromatography for anions with chemical suppression
Standards	ASTM D5827

4.2.6 Determination of sulfate in coolants

Application	Determination of sulfate in coolants
Documentation	**AN-S-041** "Sulfate in diesel engine coolant by dialysis for sample preparation"
Technology	Ion chromatography for anions with chemical suppression

Metrohm OMNIS is the system of choice for fully automated analyses.

4.3 Quality determination of lubricants

4.3.1 Determination of antioxidants in lubricating oils

Testing in-service lubricants for their remaining antioxidant content is critical to vehicle availability and for reducing operating and repair costs. Test methods such as the RPVOT (rotating pressure vessel oxidation test) are time-consuming and expensive to perform. Voltammetry with Metrohm Professional VA 884 (determination of "Remaining Useful Life") is a proven method for testing the remaining active antioxidants within minutes. Depending on the electrolytes, aromatic amine and phenolic antioxidants or inhibited phenolic antioxidants can be determined.

Application	Determination of antioxidants
Technology	Differential pulse voltammetry with the Glassy Carbon electrode
Documentation	**AN-V-220** "Remaining useful life of lubricants – Fully automated determination of residual antioxidant content by voltammetry"
Standards	ASTM D6971, ASTM D6971, ASTM D6971, ASTM D5727, ASTM D7590

4.3.2 Determination of the base number (BN = Base number)

(See: Determination of base number in hydraulic oils, 4.1.1)

4.3.3 Determination of the oxidation resistance of lubricants

Legislation, such as the U.S. Vessel General Permit, which was introduced by the Environmental Protection Agency (EPA), sets strict limits for unintentional discharges of lubricants for ships. In Europe, the recommendations of the OSPAR Commission and the Center for Environment, Fisheries and Aquaculture Science (Cefas) stipulate that lubricants must meet special requirements with regard to biodegradability.

In addition to biodegradability, the quality and stability of the oils are also important. The oxidation stability of biodegradable lubricating oils can be determined easily and directly with the Metrohm Rancimat.

Application	Oxidation stability of biodegradable lubricating oil
Technology	Rancimat method
Documentation	**AN-R-010** "Oxidation stability of biodegradable lubricating oil"

4.3.4 Determination of anions in cooling lubricants

Application	Determination of chloride, nitrite, nitrate and sulfate in cooling lubricants after inline dialysis
Technology	Determination of anions by ion chromatography with direct conductivity and UV detection after dialysis
Documentation	**AN-U-019** "Chloride, nitrite, nitrate and sulfate in cooling lubricants (conductivity and UV detection)"

4.3.5 Determination of amines in cooling lubricants

Application	Determination of dicyclohexylamine (DCHA) and methyldicyclohexylamine (MDCH) in cooling lubricants
Technology	Determination of cations by ion chromatography with direct conductivity detection after dialysis
Documentation	**AN-C-177** "Dicyclohexylamine (DCHA) and Methyldicyclohexylamine (MDCHA in cooling lubricant by inline dialysis"

4.3.6 Determination of the acid number (AN = Acid Number)

(See: Determination of the acid number (AN = Acid Number) in hydraulic oils, 4.1.2)

4.3.7 Determination of water content by Karl Fischer titration

(See: Determination of water content by Karl Fischer titration in hydraulic oils, 4.1.3)

Not only the sand , but poor engine oil quality can prevent safe advancing.

4.4 Determination of fuel quality

4.4.1 ANALYSIS OF CONVENTIONAL FUELS

4.4.1.1 Determination of the base number (BN = Base Number) in fuels

(See: Determination of the base number, BN = Base Number, in hydraulic oils, 4.1.1)

4.4.1.2 Determination of the cetane index in fuels

Application	Determination of cetane Index, density, saturation level and aromatics
Technology	Near Infrared Spectroscopy (NIRS) for liquids with NIRS XDS RapidLiquid Analyzer
Documentation	**AN-NIR-080** "Quality control of diesel fuel – Fast and easy determination of cetane index, flashpoint, CFPP, D95 and viscosity using NIRS"

4.4.1.3 Determination of inorganic chloride in fuels

In addition to acid-base titrations, titrimetric chloride determination is one of the most frequently used wet analytical analysis methods.

Application	Determination of inorganic chloride
Technology	Potentiometric titration
Documentation	**AB-130** "Potentiometrically indicated chloride titrations"
Standards	EN 15484

4.4.1.4 Determination of the hydroperoxide number in fuels

The value of the hydroperoxide number is an indication of the amount of oxidizing components present. The decomposition of the fuels leads to the formation of hydroperoxides and other oxygen-bearing compounds. The hydroperoxide number is a measure of the compounds that can be oxidized with potassium iodide.

The determination of the hydroperoxide number of gasoline is important because hydroperoxides reduce the engine octane number. Furthermore, hydroperoxides have a detrimental effect on certain components of the fuel system (e.g., elastomers).

The determination of the hydroperoxide number of diesel fuel is important, as hydroperoxides have been shown to increase the cetane number.

Technology	Potentiometric titration with the Pt Titrode
Standards	ASTM D3703

4.4.1.5 Determination of mercaptans in fuels

Mercaptan sulfur has an unpleasant odor, a detrimental effect on elastomers in the fuel system and is corrosive to the components of the fuel system.

Application	Determination of mercaptan content
Documentation	**AB-135** "Potentiometric determination of hydrogen sulfide, carbonyl sulfide and mercaptans in petroleum products"
Technology	Potentiometric titration using the Ag Titrode with sulfide coating
Standards	ASTM D3227 IP342 ISO 3012

4.4.1.6 Determination of acid content in fuels

Various acids can be present in aviation turbine fuels, either through acid treatment during the refining process or as naturally occurring organic acids. Significant acid contamination is unlikely due to the many tests performed during the various stages of refining. However, traces of acids may be present and are undesirable, as the fuel then tends to corrode metals with which it comes into contact or impair the water separation properties of the aircraft turbine fuel.

The test method is used to measure the acid traces that may be present in aircraft turbine fuel. It is not suitable for the determination of significant acid contamination.

Using a titrator with a photometric sensor – the Metrohm Optrode – to detect the endpoint ensures that titrations are always performed under the same conditions.This greatly increases the precision and reliability of results, which in turn leads to improved monitoring for your operation.

Application	Acid content in volatile solvents
Technology	Photometric titration with the Optrode
Documentation	**AN-T-203** "Acid content in volatile solvents and chemical intermediates – Objective and reliable determination in accordance with ASTM D1613"
Standards	ASTM D1613

4.4.1.7 Determination of the acid number (AN = Acid Number) in fuels

(See: Determination of acid number, AN = Acid Number, in hydraulic oils, 4.1.2)

4.4.1.8 Determination of water content by Karl Fischer titration in fuels

(See: Determination of water content by Karl Fischer titration in hydraulic oils, 4.1.3)

Take off & landing – the quality of the fuel is what really counts.

4.4.2 ANALYSIS OF BIOFUELS

The selected applications originate from the ASTM specifications for ethanol or methanol that is added to gasoline (ASTM D4806, ASTM D5797, ASTM D5798).

4.4.2.1 Determination of the conductivity of biofuels

Ethanol, bioethanol and biofuel (E85) are increasingly used as replacements for petroleum-based fuels. During storage, biofuels frequently come into contact with metallic substrates or surfaces, e.g., in drums, tanks or other containers. Excessive ion concentrations in the stored fuel promote corrosion. Monitoring the total concentration of ions present in the fuel matrix is the first step of an effective corrosion protection strategy.

A simple, fast and cost-effective method to determine the total amount of ions is to measure electrical conductivity in accordance with DIN 15938.

Application	Determination of conductivity
Technology	Direct conductivity measurement with conductivity measuring cell 6.0916.040 or 6.0918.040
Documentation	**AN-T-209** "Electrical conductivity of ethanol, bioethanol and biofuel – Fast and easy conductivity measurement in accordance with DIN 15938"
Standards	DIN 15938

4.4.2.2 Oxidation resistance of alternative fuels (biofuel)

The use of alternative fuels from renewable plant sources has become increasingly widespread in recent years and will continue to increase. In addition to alternative fuels such as ethanol, methanol or biogas (methane), fatty acid methyl esters, also known as biodiesel, RME (rapeseed oil methyl ester) or FAME (fatty acid methyl ester) have established themselves as another important renewable energy source. Fatty acid methyl esters are usually extracted from oil seeds and used either in pure form or in combination with conventional diesel fuel as a biodiesel blend in the automotive sector.

Rapeseed – sustainable raw material for biofuels

Vegetable oil is usually used for production, but fats of animal origin or waste materials from food production or processing can also be used. The oil is transesterified with methanol in a catalyzed process. This produces the methyl esters of the fatty acids present in the oil and glycerol as a by-product. Fatty acid methyl esters have only limited storage stability, since they, like all natural fats and oils, are slowly oxidized by atmospheric oxygen. The substances resulting from this can cause damage to the engine. For this reason, oxidation stability is an important quality criterion for biodiesel and is regularly determined during production. With the help of the "893 Professional Biodiesel Rancimat", this determination can be carried out easily and reliably.

Application	Determination of oxidation resistance of fatty acid methyl esters (FAME) and biodiesel blends
Technology	Rancimat method using the Biodiesel Rancimat
Documentation	**AN-R-009** "Oxidation stability of fatty acid methyl esters (FAME, biodiesel)"
Standards	EN 15751

4.4.2.3 Determination of pHe (biofuels)

pHe is a measure of acid strength in alcohol fuels and ethanol. It can be used as a predictor of the corrosion potential of an ethanol fuel. The determination of pHe is preferred over total acidity, since total acidity depends on the contribution of weak acids (e.g., carbonic acid) and of strong acids (e.g., sulphuric acid). Acid strength is also an important parameter in order to reduce the risk of motor failure.

The pHe value is an indicator of acid strength and indicates the presence of strong acids or bases in ethanol. In Europe, ethanol is used as a blending component in gasoline and must have a pH between 6.5 and 9.0.

Application	Determination of pHe of fuels based on (bio)ethanol
Technology	pH measurement with the EtOH-Trode
Documentation	a) **AN-T-173** "pHe value of denatured ethanol fuel – Fast and accurate measurement in accordance with ASTM D6423" b) **AN-T-183** "Ethanol as an admixture for gasoline – Determination of pHe value in accordance with EN 15490"
Standards	a) ASTM D6423 b) EN 15490

4.4.2.4 Determination of inorganic sulfate in biofuels

Ethanol is used as a blending component of gasoline. When ethanol-containing fuel is burned, sulfates can contribute to sulphuric acid emissions. Sulfates also show up in deposits that clog the filter and in deposits in the fuel injection. The admissibility of the use of ethanol depends on the sulfate content. The sulfate content measured with the test method in accordance with ASTM D7318 can be used as a measure of the acceptance of ethanol as a fuel for spark-ignition motor vehicles.

Application	Determination of inorganic sulfate content
Technology	Potentiometric titration with Pb ISE and Ag/AgCl reference electrode
Documentation	**Poster 8.000.6020** "Titrimetric analysis of biofuels"
Standards	ASTM D7318

4.4.2.5 Determination of the acid content of biofuels

Denatured fuel ethanol can contain additives such as corrosion inhibitors and cleaning agents as well as impurities from production that can affect the acidity of the finished ethanol fuel. Highly diluted aqueous solutions of organic acids with low molecular weight, such as acetic acid, are highly corrosive for many metals. It is important to keep these acids at a very low level.

The test method in accordance with ASTM D7795 quantitatively measures the acid content in ethanol or ethanol mixtures. The acceptable acid content in ethanol or ethanol mixtures may vary depending on the specification but is generally below 200 mg/kg (ppm). Knowledge of the acid content may be required to determine if the product quality is within specification.

Application	Determination of the acid content of (bio)ethanol-based fuels or biodiesel
Technology	Photometric titration with the Optrode
Documentation	a) **AN-T-199** "Photometric determination of the acid content of ethanol in accordance with ASTM D7795" b) **Poster 8.000.6020** "Titrimetric analysis of biofuels"
Standards	a) D7795 b) EN 15491

4.4.2.6 Determination of water content in biodiesel

Application	Determination of water content in fuels
Technology	Coulometric Karl Fischer titration
Documentation	**8.026.5013** Monograph "Water determination by Karl Fischer titration" **Poster 8.000.6077** "Water determination in biodiesel by Karl Fischer titration according to EN ISO 12937"
Standards	ASTM D6304, IP 471, EN ISO 12937 (Biodiesel)

4.4.2.7 Determination of water content in ethanol-fuel mixtures

Mixtures of fuel ethanol and hydrocarbon fuel have a limited solubility for water, which in turn depends on the temperature and the ratio of ethanol to hydrocarbon. Good handling practices are important during mixing, storage and transportation of fuel to avoid water entry. High water concentrations can cause turbidity or phase separation in ethanol and hydrocarbon mixtures and result in freezing problems at low temperatures. Water is also associated with corrosion and clogging of filters.

Application	Determination of water content according to Karl Fischer
Technology	Coulometric water content determination (0.004% – 1.63%) Volumetric water content determination (0.02 – 5.41%) in accordance with ASTM D7923
Documentation	a) **AB-077** "Volumetric Karl Fischer water content determination – Tips and tricks for volumetric Karl Fischer titration" b) **AB-137** "Coulometric Karl Fischer water content determination"
Technology	Volumetric or coulometric Karl Fischer titration
Standards	a) ASTM E203 b) ASTM E1064 ASTM D7923

Monitoring the air to breath is vital on submarines

5. Air

5.1 Ensuring the quality of breathing air on submarines

5.1.1 Analysis of amine-containing washing solutions

To remove the exhaled carbon dioxide (CO_2), scrubber solutions containing amines are used on submarines. These solutions bind the CO_2 and remove it from the breathing air. The correct functioning of the scrubber solutions must be continuously monitored.

Application	Ensuring the quality of breathing air
Application	Online analysis of amine-containing scrubber solutions
Technology	Potentiometric acid-base titration
Standards	CO_2 < 0.5%: NIOSH (National Institute for Occupational Safety and Health)

6. Water

6.1 Monitoring of boiler feed and cooling water monitoring

6.1.1 Determination of conductivity

This method of measurement is suitable for detecting impurities and, in some cases, for quantitative measurement of ionic components dissolved in water. These include dissolved electrolytes in natural and purified water, such as boiler water, boiler feed water, cooling water, and salt and brackish water.

Their concentration can range from trace levels in pure water to significant concentrations in condensed steam (see test methods D2186 and D4519) or pure saline solutions.

If the main interest in applying conductivity methods is to determine the purity of steam, these test methods can also be used to verify the accuracy of water analyses.

Application	Determination of conductivity
Technology	Direct measurement with conductivity measuring cell
Documentation	**AB-102** "Conductometry" **AB-178** "Fully automated water analysis" **AN-T-205** "Fully automated water analysis with OMNIS"
Standards	ASTM D1125, EPA 120.1, ISO 7888, EN 27888

6.1.2 Determination of pH at low conductivity

pH measurement of water with low conductivity is widely used in power plant water and steam condensate samples to prevent corrosion and scale formation. It can also be used in ultrapure water treatment systems between multiple membranes in order to optimize performance.

Ultrapure water is to a great extent unbuffered, and small amounts of impurities can significantly alter pH. In particular, ultrapure water quickly absorbs carbon dioxide from the atmosphere, which lowers the pH of the sample. The special sample container and the associated pH measurement method minimize the exposure of the pure water sample to the atmosphere.

Application	Monitoring of cooling water
Application	Determination of pH
Technology	pH measurement, direct measurement with Aquatrode plus
Documentation	**AB-188** "pH measurement technology" **AB-178** "Fully automated water analysis"
Standards	ASTM D5464

6.1.3 Determination of pH at regular conductivity

The pH of water is a critical parameter that affects the solubility of trace minerals and water's ability to form scale or cause metal corrosion. A change in pH thereby also provides information on the effectiveness of added corrosion inhibitors. The neutral point of chemically pure water has a pH of 7.0 at 25°C but varies depending on the temperature and ionic strength of the sample. Pure water in equilibrium with the air has a pH of about 5.5. Most natural, uncontaminated waters are between pH 6 and pH 9.

Application	Determination of pH
Technology	pH measurement, direct measurement with Aquatrode plus
Documentation	**AB-188** "pH measurement technology" **AB-178** "Fully automated water analysis"
Standards	ASTM D1293, ASTM D5464, EPA 150.2, EN ISO 10523

6.1.4 Determination of water hardness

Hardeners in the water, especially calcium and magnesium, are the main cause of calcification of pipes and pipelines, which often leads to failures and loss of process efficiency due to clogging or loss of heat transfer or both.

Hardness is caused by all polyvalent cations but mainly by calcium and magnesium. All other polyvalent cations are rarely present in more than trace amounts. The term hardness was originally used for water that is difficult to use for washing purposes with because it required using a lot of soap. In most water types, this undesirable property is directly related to the calcium and magnesium content.

Application	Determination of water hardness
Technology	a) Potentiometric titration with Ca ISE b) Photometric titration with the Optrode
Documentation	a, b) **AB-125** "Simultaneous determination of calcium and magnesium as well as alkalinity by complexometric titration with potentiometric or photometric indication in water and beverage samples" a) **AB-178** "Fully automated water analysis" a) **AN-T-205** "Fully automated water analysis with OMNIS" b) **AN-T-084** "Fully automatic determination of total calcium and magnesium hardness of water samples by photometric titration"
Standards	ASTM D511, ASTM D1126, EPA 130.2, EPA 215.2, ISO 6058, ISO 059

6.1.5 Determination of alkalinity

Acidity and alkalinity measurements are used to determine possible required chemical treatment stages, e.g., to control/avoid scale and corrosion.

Acidity and alkalinity values are crucial for determining the solubility of some metals, the toxicity of some metals and the buffer capacity of some waters.

Application	Determination of alkalinity
Technology	Endpoint titration to predefined pH values with Aquatrode plus
Documentation	**AB-178** "Fully automated water analysis" **AN-T-205** "Fully automated water analysis with OMNIS"
Standards	ASTM D1067, EPA 310.1, EN ISO 9963-1, EN ISO 9963-2

6.1.6 Determination of anions and cations

Measurement of anions and cations in cooling water and boiler feed water provides important information about corrosion, corrosion prevention and the quality of the water used.

Application	Determination of anions and cations
Technology	Ion chromatography with chemical suppression and conductivity detection (anions); Non-suppressed ion chromatography with conductivity detection (cations)
Documentation	**Brochure 8.000.5148** "Power plant analytics"
Standards	EPA 300.1

6.2 Drinking water safety

Soldiers depend on clean drinking water to fulfill their mission and maintain their performance and endurance, anytime and anywhere. In addition to the analysis of standard parameters such as calcium, magnesium, pH, chloride, etc., Metrohm offers complete solutions for highly sensitive trace level analysis of toxic heavy metals (uranium, chromium, mercury, arsenic, etc.) as well as other contaminants.

With instruments for ion chromatography, voltammetry and titration, Metrohm offers robust solutions that are easy to use and deliver accurate results within minutes.

For the targeted determination of individual ingredients, chemical analysis offers procedures that can be conveniently used as a matter of routine. A closer look at individual parameters is of fundamental importance for the determination of highly toxic substances: Cyanide has a fatal effect in the milligram range, oxohalides cause lasting damage in the microgram range and heavy metals such as plutonium and uranium develop their harmful effect in the nanogram (ppt) range.

6.2.1 PH AND CONDUCTIVITY MEASUREMENT

6.2.1.1 Determination of the pH value in drinking water

pH is arguably the most commonly measured parameter of aqueous solutions – from mobile measurement in drinking water, surface water, groundwater and wastewater to precise determination of the pH of water for pharmaceutical use. Wherever pH is determined, Metrohm offers the optimal solution for every application.

Application	pH measurement
Technology	Direct measurement
Documentation	**AN-T-073** "Fully automated determination of conductivity, pH and alkalinity in tap water after sample preparation" **AN-T-205** "Fully automated water analysis with OMNIS"
Standards	EPA 150.1, DIN 38404-5

6.2.1.2 Determination of the conductivity of drinking water

Application	Measurement of conductivity
Technology	Direct measurement
Documentation	**AN-T-073** "Fully automated determination of conductivity, pH and alkalinity in tap water after sample preparation" **AN-T-205** "Fully automated water analysis with OMNIS"
Standards	EPA 120.1, DIN EN 27888

6.2.2 DETERMINATION OF SUM PARAMETERS BY TITRATION

6.2.2.1 Free chlorine and residual chlorine content in drinking water

Chlorine is often added to the drinking water in low concentrations for disinfection purposes. As chlorine is highly toxic, organisms such as bacteria are killed, and the occurrence of waterborne diseases such as cholera is prevented. Chlorine is toxic not only to microorganisms but also to humans. Depending on the reactivity and concentration of the chlorine, toxic disinfection by-products may be formed and released. The main reason for toxicity is the fact that chlorine can react with other organic compounds and form disinfection by-products (DBPs) such as trichloromethane and chloroacetic acid.

The chlorine concentration in drinking water must therefore be precisely controlled and monitored in order to reliably comply with the limit values specified by regulations, ordinances and statutory provisions such as the German Drinking Water Ordinance.

Application	Determination of free chlorine and residual chlorine content
Technology	Potentiometric titration with the Pt Titrode
Documentation	**AB-249** "Determination of free chlorine and residual chlorine content in accordance with DIN EN ISO 7393-1 and APHA 4500-Cl"
Standards	EN ISO 7393-1 APHA 4500-Cl Methode B APHA 4500-Cl Methode I

6.2.2.2 Determination of the permanganate index by titration

(in accordance with DIN EN ISO 8467 and CSB DIN 38409-12)

With regard to the oxidation force of the oxidants used, a distinction is made between the permanganate index and chemical oxygen demand (COD). Whereas the permanganate index is the more meaningful parameter for samples with little to low load, the COD is suitable for samples with high load.

The permanganate index serves in the broader sense as a measure for assessing the organic-chemical load in water with little or no load, such as drinking water samples.

The permanganate index is used to determine the easily oxidizable proportion of organic substances in the water.

Application	Determination of the permanganate index
Technology	Potentiometric titration with the Pt Titrode
Documentation	**AN-T-204** "Permanganate index in water – Fully automated determination in accordance with GB/T 11892" **AN-T-094** "Fully automated determination of the permanganate index in accordance with EN ISO 8467"
Standards	GB/T 11892, EN ISO 8467, DIN EN ISO 8467, CSB DIN 38409-12

Clean drinking water forms the backbone of operational capability.

6.2.2.3 Determination of oxygen content in drinking water

In the drinking water supply, a higher DO content (DO = Dissolved Oxygen) is desirable because it improves the taste of the drinking water. If the DO content is too low, the taste experience can be perceived as bland.

Application	Determination of oxygen content
Technology	Measurement of luminescence
Documentation	**AN-I-030** "Dissolved oxygen in tap water – Fast online determination using an optical sensor in accordance with ISO 17289"
Standards	ISO 17289

6.2.2.4 Determination of the chemical oxygen demand

Chemical oxygen demand (COD) is a measure of the sum of the substances oxidizable by chromate in a given volume of water.

In wastewater treatment plants, COD is regarded as a meaningful guide parameter for assessing the clarification performance and thus the quality of the drinking water.

Application	Determination of chemical oxygen demand (COD)
Technology	Potentiometric titration with the Au ring electrode
Documentation	**AB-178** "Fully automated water analysis"
Standards	DIN 38409-44, ASTM D1252

6.2.2.5 Determination of water hardness

(calcium and magnesium in accordance with to DIN 38406-3)

In the case of water hardness, a distinction is made between temporary (carbonate hardness) and permanent (sulfate hardness). Another important parameter is the total hardness, which indicates the sum of the alkaline earth metal cations and is made up approximately of the sum of the calcium and magnesium hardness.

pH and conductivity measurement in the field. Photo: German Armed Forces

Application	Determination of water hardness
Technology	Potentiometric titration with the combined Ca ISE
Documentation	**AB-125** "Simultaneous determination of calcium, magnesium and alkalinity by complexometric titration with potentiometric or photometric indication in water and beverage samples" **AB-178** "Fully automated water analysis"
Standards	DIN 38406-3

6.2.3 DETERMINATION OF INDIVIDUAL IONS AND MOLECULES BY ION CHROMATOGRAPHY

6.2.3.1 Determination of anions

Even though their analytical performance is very high, Metrohm's robust IC systems are easy to operate, whether in stationary laboratories, mobile field laboratories, on ships or in aircraft. For operation, only the power supply must be available via a power outlet. The IC systems can determine standard anions safely and quickly.

Chlorate, chlorite and bromate are by-products that can be produced by oxidization of the halides present in the water when disinfecting drinking water and mineral water. Due to their carcinogenic and thyroid-damaging properties, the German Drinking Water Ordinance prescribes compliance with limit values for these substances. Their concentration in drinking water must be checked for compliance with the specified limit values in accordance with the provisions of the Drinking Water Ordinance.

Ion chromatography (IC) can be used to determine these undesirable by-products as well as all other anions and cations present in the water. A glance at the label of a bottle of mineral water shows the measured values.

Application	Determination of anions
Technology	Ion chromatography for anions with chemical suppression and conductivity detection (anions)

Metrohm IC devices: ready for use in a mobile field laboratory

Documentation	**AN-S-236** "Drinking water quality in accordance with EPA 300.1 – Combination of Part A and B of EPA Method 300.1 in an IC analysis"
Standards	EPA 300.1, EN ISO 10304-1, EN ISO 10304-4

6.2.3.2 Determination of bromate

Bromate is a disinfection by-product produced by ozonization during drinking water treatment. It is undesirable because it is suspected of causing cancer in humans and of damaging the thyroid gland. The limit value contained in the German Drinking Water Ordinance must be monitored in accordance with the provisions of the Drinking Water Ordinance.

Application	Determination of bromate in drinking water
Technology	Ion chromatography for anions with post-column derivatization and UV detection
Documentation	**AN-U-051** "Trace analysis of bromate in drinking water –Determination in accordance with ISO 11206 using triiodide post-column derivatization and subsequent UV detection"
Standards	ISO 11206, EPA 326

6.2.3.3 Determination of cyanide

Due to cyanide's high toxicity, the determination of cyanide in drinking water is very important. The limit value contained in the German Drinking Water Ordinance must be monitored in accordance with the provisions of the Drinking Water Ordinance.

Depending on the type of water sample, cyanide determination can be performed quickly and reliably using ion chromatography (IC), voltammetry (VA) or titration.

Application	Determination of cyanide
Technology	Ion chromatography for anions with direct conductivity detection
Documentation	**AN-N-068** "Cyanide in waste water"
Application	**Determination of cyanide**
Technology	Ion chromatography for anions with amperometric detection
Documentation	**AN-P-052 "Trace analysis of cyanide and sulfide in aqueous samples – Amperometric determination in DC mode after ion chromatographic separation"**
Application	**Determination of free cyanide**
Technology	Polarography
Documentation	**AB-110** "Determination of free cyanide by polarography"
Application	**Determination of cyanide**
Technology	Potentiometric titration with Ag Titrode (precipitation titration)
Documentation	**AB-046** "Potentiometric cyanide determination"

6.2.3.4 Determination of cations

Drinking water analyses and thus the determination of cations are regulated by standards such as ISO 14911. Ion chromatography delivers reliable results.

Anwendung	Drinking water safety
Technology	Ion chromatography for cations using conductivity detection
Documentation	**AN-C-135** "Cations in tap water using the Metrosep C4 – 150/4.0 column in accordance with ISO 14911"
Standards	ISO 14911

6.2.3.5 Determination of perchlorate

Perchlorate often enters the water from anthropogenic sources such as fertilizers, fireworks, rocket fuel, etc. Trace analysis of perchlorate in water samples is a critical application.

Anwendung	Determination of perchlorate in drinking water
Technology	Ion chromatography for anions using conductivity detection after chemical suppression
Documentation	**AN-S-342** "Determination of perchlorate in drinking water in accordance with ISO 19340 using Annex B"

6.2.3.6 Determination of chromium (VI)

Application	Determination of chromium (VI)
Technology	Anion chromatography with UV detection
Documentation	**Poster 8.000.6087** "Determination of chrome (VI) in drinking water according to the U.S. Environmental Protection Agency (EPA)" **AN-U-057** "Chromate in drinking water using ion chromatography and post-column reaction with UV/VIS detection in accordance with EPA method 218.7"
Standards	EPA 218.7

6.2.4 DETERMINATION OF INDIVIDUAL IONS AND MOLECULES BY VOLTAMMETRY

Heavy metals can be determined at very low concentrations by voltammetry (VA). These include the "bad four" i.e., zinc, cadmium, lead, and copper, which are analyzed in accordance with DIN 38406-16.

VA systems are suitable for mobile use. They have proven themselves in deployments by the German Armed Forces, including in Afghanistan, and have protected soldiers agaiinst the danger of heavy metals in drinking water.

VA systems feature impressive low equipment requirements, low investment and operating costs, easy sample preparation and short analysis times as well as high accuracy and sensitivity of the measurements.

A particular advantage is the possibility of specification analysis. The analyte is not determined in its entirety, but in the various oxidation stages and binding forms present, as in the case of Cr(III) and Cr(VI) – only chromium in the oxidation stage (VI) is toxic.

VA systems can also be used for ultratrace analysis of uranium.

6.2.4.1 Determination of arsenic

Application	Determination of arsenic (total) and arsenic (III)
Technology	Anodic Stripping Voltammetry with scTrace Gold electrode
Documentation	**AN-V-416** "Determination of arsenic in water using scTrace Gold"

6.2.4.2 Determination of cadmium and lead

Application	Determination of cadmium and lead
Technology	Voltammetry
Documentation	**AN-V-221** "Cadmium and lead in drinking water – simultaneous determination by voltammetry on a bi-drip electrode"

6.2.4.3 Determination of chromium

Application	Determination of chromium
Technology	Voltammetry
Documentation	**AN-V-227** "Chrome(VI) in drinking water – Highly sensitive determination on the Glassy Carbon electrode modified with a mercury film (DTPA method)" **AN-V-230** "Chrome(VI)in drinking water – Sensitive determination on scTRACE Gold modified with a mercury film (DTPA method)"

6.2.4.4 Determination of cyanide

(see also Ion Chromatography)

Application	Determination of free cyanide
Technology	Polarography
Documentation	**AB-110** "Determination of free cyanide by polarography"

6.2.4.5 Determination of uranium

Application	Determination of uranium
Technology	Voltammetry
Documentation	**AN-V-045** "Uranium in drinking water" **AB-430** "Determination of uranium by adsorptive stripping voltammetry in accordance with DIN 38406-17"
Standards	DIN 38406-17

6.2.4.6 Determination of zinc, cadmium, lead and copper

Application	Determination of zinc, cadmium, lead and copper in waste water
Technology	Voltammetry
Documentation	**AN-V-083** "Determination of zinc, cadmium, lead and copper in waste water after UV digestion"

6.3 Analysis of antiseptics and disinfectants

Disinfectants play an important role worldwide. Especially in times of widespread illness, it is essential to protect people and animals from harmful bacteria, viruses or fungi. Animal diseases such as bird or swine flu or communicable viruses such as COVID-19 can cause billions of dollars of economic damage and even destroy entire industries. Calcium hypochlorite "C8", sodium hypochlorite and sodium chloride are effectively used as disinfectants for water and surfaces. They are widely available and cost-effective. However, it is important to perform the correct dilution in order to achieve the most efficient disinfection.

The World Health Organization (WHO) recommends (depending on the application) concentrations in disinfectants of 1000–5000 mg/L NaOCl and up to 200 g/L NaCl

6.3.1 Determination of bleach (sodium hypochlorite in aqueous solutions)

Application	Analysis of disinfectants
Application	Determination of bleach (sodium hypochlorite in aqueous solutions) sodium hypochlorite
Technology	Potentiometric or thermometric titration with the Pt Titrode or Thermoprobe
Documentation	**AN-H-019** "Determination of chlorine in household bleach"
Technology	ASTM D2022

6.3.2 Determination of sodium hypochlorite and sodium chloride

Application	Determination of sodium hypochlorite and sodium chloride –Reliable all-in-one determination of sodium hypochlorite and sodium chloride
Technology	Potentiometric titration with the Ag Titrode (argentometric titration)
Documentation	**AN-T-217** "Hypochlorite and sodium chloride in disinfectants – Reliable combined determination via argentometric titration"
Standards	DIN 38408-3

6.3.3 Determination of ozone

Water treatment with ozone (O_3) is a common method of disinfection.

Application	Determination of ozone (O_3)
Technology	Potentiometric titration with the double Pt plate electrode
Documentation	**AN-T-213** "Simple determination of ozone in water"
Standards	DIN 38408-3

6.3.4 Determination of hydrogen peroxide

Peroxides are often used for disinfection and water treatment due to their antiseptic properties. Lower concentrations between 0.3-3% are used in households, while higher concentrations can be used for sterilization purposes.

Application	Determination of hydrogen peroxide
Technology	Potentiometric titration with the combined Pt ring electrode
Documentation	**AN-T-025** "Hydrogen peroxide content in aqueous solutions – Reliable and cost-effective determination in accordance with ASTM D2180"
Standards	ASTM D2180

Explosives and propellants must be checked at regular intervals.

7. Explosives

7.1 Quality control of explosives

In the field of quality control of propellants and explosives Metrohm has a wealth of analytical know-how and the right experts to run these applications professionally.. A key application here is the highly sensitive determination of moisture levels. With proven solutions for Karl Fischer titration, Metrohm offers a primary method with which water concentrations can be determined simply and safely in the ppm range – fully automatically.

7.1.1 Determination of water content in explosives

To ensure safe combustion or explosive properties, the water content of the propellants and explosives must be checked at regular intervals.

Application	Determination of water content in explosives
Technology	Volumetric and coulometric Karl Fischer titration (KF) or by Near Infrared Spectroscopy (NIRS)
Documentation	**AN-K-009** "Water in explosive pellets" **AN-K-013** "Water in organic peroxides" **AN-K-064** "Determination of water in dimethyl ether (DME)" **AN-NIR-064** "Quality control of ammonium nitrate – Fast and non-destructive moisture determination"

7.1.2 Determination of sodium hydrogen carbonate in fire extinguishing powder

Carbonate is the most important contaminant in the fire-extinguishing powder based on sodium hydrogen carbonate (sodium bicarbonate). A selective method is therefore required for the test. Separation of the two species carbonate – hydrogen carbonate by ion chromatography is not possible, as the eluent changes the ratio of carbonate and hydrogen carbonate and distorts the result. Due to their different pKa values, carbonate and hydrogen carbonate can be determined selectively by titration.

Application	Determination of sodium hydrogen carbonate in fire-extinguishing powders
Technology	Potentiometric titration with the Unitrode
Documentation	**AN-T-210** "Analysis of potassium carbonate and potassium hydrogen carbonate – Reliable and selective determination of both substances"

7.1.3 Water content in nitro compounds and specialty chemicals

Nitro compounds and *specialty chemicals* must meet a number of quality requirements. One of these quality parameters that appears in almost all certificates of analysis and specifications is moisture content. As an alternative to Karl Fischer titration, near infrared spectroscopy (NIRS) can be used to determine moisture content. With this method, samples can be analyzed without preparation and without the use of chemicals.

Application	Determination of water content in nitro compounds
Technology	Near Infrared Spectroscopy (NIRS)
Documentation	**AN-NIR-064** "Quality control of ammonium nitrate – Fast and non-destructive moisture determination"

7.1.4 Water content in ammonium nitrate

Application	Determination of water content in ammonium nitrate
Technology	Near Infrared Spectroscopy (NIRS)
Documentation	**AN-NIR-064** "Quality control of ammonium nitrate – Fast and non-destructive moisture determination"»

7.1.5 Determination of picric acid and stifnic acid

Application	Quantification of picric acid and stifnic acid
Technology	Determination by near infrared spectroscopy (NIRS)

7.1.6 Determination of tetrazene in ignition mixtures

Application	Quality control of explosives
Application	Quantification of tetrazene in ignition mixtures
Technology	Determination by near infrared spectroscopy (NIRS)

7.1.7 Determination of uranium in solution, in uranium hexafluoride and in solids

The determination of uranium in accordance with ASTM C1267 can be carried out for a wide variety of products, uranium hexafluoride or uranium ore concentrate as well as fuels and scrap. This method determines 20 to 200 mg of uranium after the material has been dissolved. The analysis is tolerant to most metal contaminants commonly found in products and fuels and does not require any special equipment.

This method is also important for quality control in nuclear fuels.

Application	Quantification of uranium
Technology	Potentiometric titration with the combined Pt ring electrode
Documentation	**AB-223** "Fully automated determination of uranium"
Standards	ASTM C1267 ISO 7097-1

7.2 Determination of individual explosives

The determination of explosives is of central importance, for example, in explosive ordnance dsiposal (EOD). Analysis of unknown substances directly at the location where they are found provides an important indication of whether they are hazardous or not. In the area of forensics, too, the detection of explosives provides direct evidence of their provenance.

Metrohm Raman spectrometers such as the MIRA DS XTR are specially designed for explosives analysis. They work with low energy (< 50 mW) as standard and use the patented "Orbital Raster Scanning" (ORS) process, which significantly reduces the irradiated laser energy per area. The measurement can be made with a time delay or remotely. Due to their remote controllability and low weight, Metrohm Raman spectrometers are especially suitable for use on robots and with drones.

Explosives search in rough terrain: MIRA XTR DS in use with the quadrupedal robot from ANYbotics.

Application	Qualitative determination of explosives
Technology	Raman spectroscopy with MIRA DS XTR @ 785 nm
Documentation	**Whitepaper WP-027** "Smart Acquire – Automated material identification using Raman spectroscopy for security and defense professionals" **Whitepaper WP-072** "Fluorescence-free material identification with MIRA XTR DS at 785 nm"
Standards	Device complies with MIL-STD 810G
Application	**Forensic investigation analysis of explosives**
Technology	Ion chromatography for anions using chemical suppression and conductivity detection
Documentation	**AN-S-305** "Forensic investigation analysis – Determination of low levels of chlorate, thiosulfate, thiocyanate and perchlorate in addition to important anions in explosives and residues"

Please contact your local Metrohm representative for the list of determinable explosives.

7.3 Determination of chemical warfare agents and their source materials

Following the attacks in New York on September 11, 2001 and the attacks with biological (anthrax) and chemical weapons (novitschok), the development of analytical methods for the determination of chemical and biological warfare agents has made great progress. Raman spectroscopy plays a central role in this, as a large number of substances can be determined quickly and reliably without the user having to come into direct contact with them. The Raman spectrometer from Metrohm – namely the MIRA XTR DS – are small, handy and high-performance devices and can determine up to 20,000 substances safely and reliably. Fluorescent samples are no longer a problem, so measurements can be performed with a low wavelength of only 785 nm.

MIRA XTR DS enables the contact-free and safe determination of chemicals and hazardous substances.

Anwendung	Determination of chemical warfare agents and their starting substances
Application	Determining chemical warfare agents
Documentation	**Whitepaper WP-72** "Fluorescence-free material identification with the MIRA XTR DS at 785 nm"
Standards	Device complies with MIL-STD 810G

Please contact your local Metrohm representative for the list of determinable warfare agents and their source materials.

Precise analytics ensure quality in production and safety in application.

8. Quality control of pharmaceuticals

Due to years of experience in application development for pharmaceutical analytics, Metrohm is a competent partner for industry, public authorities and health services.

Metrohm's expertise encompasses hundreds of applications that can be used to determine the identity and concentration of active pharmaceutical ingredients (API), contaminants as well as counterfeits (counterfeit detection). The methods used to carry out these applications are often standardized (USP, EN, ISO) and range from pH measurement, titration and ion chromatography to spectroscopic methods for real-time in-field analysis.

In terms of the quality and safety of pharmaceuticals, authorities around the world place very high demands on the pharmaceutical industry. These are documented in pharmacopeias in the form of official collections of recognized pharmaceutical rules. As a legal means of consumer protection, they ensure the safe use of medicinal products.

Only the measurement and testing procedures used in the context of drug testing identify a drug and decide on its release. Reliable equipment and methods are required to ensure these high quality and safety standards.

Application	Pharmaceutical Quality Control
Documentation	**Brochure 8.000.5139** "Pharmaceutical Analytics – Quality Control of Pharmaceuticals"

Subject to change | Layout by RTS Rieger Team, printed in Switzerland by Metrohm AG, CH-9101 Herisau