

Water Analysis



Quality control of water



Metrohm...

- is the global market leader in titration
- offers a complete portfolio for NIR and Raman analysis, in addition to all of the methods of ion analyses – titration, voltammetry, and ion chromatography
- is a Swiss company and manufactures exclusively in Switzerland
- grants a 3-year instrument warranty and a 10-year warranty on chemical suppressors for anion chromatography
- provides you with unparalleled application expertise
- offers you more than 1800 applications free of charge
- supports you with 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 water analysis

Harmful substances in water

Water is the source and basis of all life. It is essential for metabolism and is our most important foodstuff. As a solvent and transporting agent it carries not only the vital minerals and nutrients, but also, increasingly, harmful pollutants, which bioaccumulate in aquatic or terrestrial organisms. Within the context of quality control and risk assessment there is a need in the water laboratory for cost-effective and fast instruments and methods that can deal with the ever more complex spectrum of harmful substances, the increasing throughput of samples and the decreasing detection limits.

You can count on our support

As a leading manufacturer of instruments for chemical analysis, we are aware of these challenges. For this reason, Metrohm offers you not only the most advanced instruments, but complete solutions for very specific analytical issues. Your Metrohm contacts are competent specialists, who develop customized applications for you and provide you with professional support in all matters concerning water analysis.

Discover on the following pages what analytical solutions Metrohm is able to offer the water analysis sector in general and you in particular, to ensure the quality and reliability of your work. Challenge us!



There is more than we'd like in water ...

04

Thales of Miletus (ca. 625–545 BC), one of the first Greek natural philosophers and one of the «Seven Wise Men», considered water as the source of all things, to which everything returns. This perception takes on a completely new meaning in view of the 1700 substances, mainly of anthropogenic origin, that can today be detected in water. As a source of food and energy, during use in irrigation, as a solvent, cleaning agent, or coolant, and also as a means of transportation and discharge system for effluents, water becomes contaminated with fertilizers, pesticides, drugs, hormones, heavy-metal compounds, bodycare and synthetic products. Because of the

associated health risks, the World Health Organization (WHO) has issued guideline values for about 200 substances found in water. These guideline values, together with the hydrogeological conditions of the various countries, form the basis for the setting of country-specific limits. That is why water is the subject of a host of laws, regulations, and standards in most countries.

For many of these standards and regulations, Metrohm offers robust, reliable, and very precise analyzers and analytical methods.



Selected standards relating to water analysis

The standards listed below describe the measurement of conductivity and pH value as well as the determination of anions and cations in various types of water. Metrohm analyzers meet all the minimum requirements and limits set in the respective standards. Whilst some standards

describe simultaneous determination of several analytes (e.g., EPA 300.1), one and the same analyte (e.g., chloride) can also be determined using different analytical techniques, depending on the prescribed limit and the sample matrix.

05

Parameter	Standard	Matrix	Method	Page
pH value	DIN 38404-5	All types of water	pH measurement	6
	EPA 150.1	Acid rain Drinking water Seawater Wastewater	pH measurement	
	USP<791>	Pharmaceutical water	pH measurement	
Conductivity	DIN EN 27888	Drinking water	Conductivity measurement	7
	EPA 120.1	Acid rain Drinking water Seawater Wastewater	Conductivity measurement	
	USP<645>	Pharmaceutical water	Conductivity measurement	
Total hardness Ca, Mg	EPA 130.2	Drinking water Wastewater	Titration	8
	EN ISO 9963	Drinking water Wastewater		
	DIN 38406-3	Drinking water Wastewater		
Acid and base capacity	DIN 38409-7	All types of water	Titration	
Alkalinity as CaCO ₃	EPA 310.1	Drinking water Seawater Wastewater	Titration	8
Cl ⁻	DIN 38405-1	Drinking water Wastewater	Titration	8
Permanganate index	DIN EN ISO 8467	Drinking water	Titration	9
Chemical oxygen demand (COD)	DIN 38409-44 ASTM D1252	Sea water Wastewater	Titration	10
Anions, e.g., F ⁻ , Cl ⁻ , Br ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , etc.	EPA 300.1, Part A	Drinking water Wastewater	Ion chromatography	12
Oxohalides	EPA 300.1, Part B	Drinking water Wastewater	Ion chromatography	12
	EPA 317.0	Drinking water		
	EPA 326.0	Drinking water		
	DIN EN ISO 11206	Drinking water		
	ASTM D6581	Drinking water		
Cations, e.g., Li ⁺ , Na ⁺ , K ⁺ , NH ₄ ⁺ , Mg ²⁺ , Ca ²⁺ , etc.	ASTM D6919	Drinking water Ultrapure water	Ion chromatography	14
	ISO 14911	Ultrapure water Wastewater		
Zn, Cd, Pb, Cu, Tl, Ni, Co	DIN 38406-16	Drinking water Wastewater	Voltammetry	17
Uranium	DIN 38406-17	Groundwater Raw water Drinking water	Voltammetry	
CN ⁻	Sample preparation acc. to DIN 38405-13	Wastewater Drinking water	Voltammetry	18
Cd, Pb, Cu, Fe ^{II} /Fe ^{III} , Cr ^{VI}	–	Seawater	Voltammetry	
Cu, Fe, Zn, Co	–	Boiler feed water Cooling water	Voltammetry	19
pH value Conductivity Anions Cations	Various	All types of water	(Titration and Ion Chromatography, TitrIC; Voltammetry and Ion Chromatography, VoltIC)	20
pH value, conductivity, TOC, and various parameters that can be determined by titration, IC, voltammetry, or spectroscopy	Process-dependent specifications	Wastewater Cooling water Process water Drinking water	Process analysis	24

pH and conductivity measurement

06

The pH value is probably the most frequently measured parameter of aqueous solutions – ranging from mobile measurement in drinking water, surface water, ground-water, and wastewater through to precise measurement of the pH value of water for pharmaceutical use. Wherever pH values are determined, Metrohm offers the ideal solution for every application.

Drinking water

«Two-in-one» – for indoors and outdoors

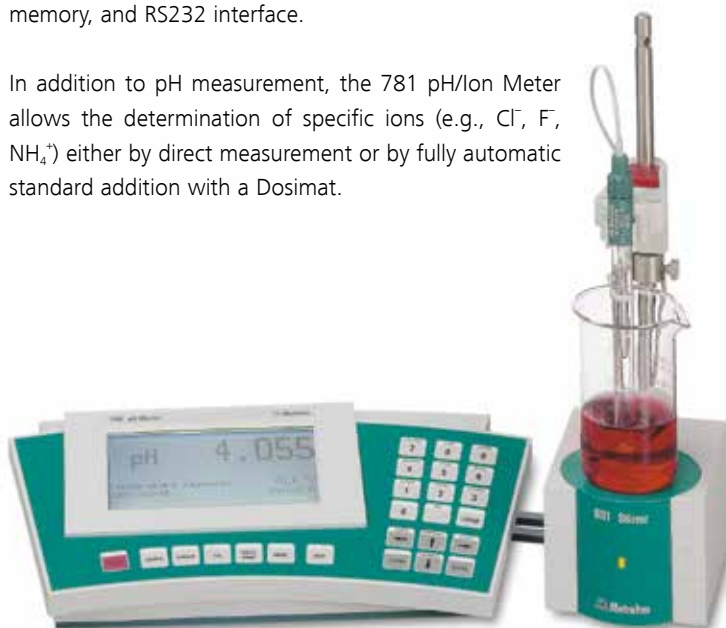
The new Metrohm meters are «two in one»: precision instruments for measurements in the laboratory and robust companions for mobile use in the field and at the process. Optional battery operation makes the new meters independent of a power grid. They can even be recharged on the road with the use of a cigarette lighter car adapter. Results can be saved with the press of a button and can be uploaded onto the PC at the office.

The 914 pH/Conductometer measures pH and conductivity in parallel; the 913 pH Meter can simultaneously determine two pH values.

pH value, chloride, fluoride, and ammonium with 780 pH Meter or 781 pH/Ion Meter

The 780 pH Meter is the first choice if you wish to obtain highly precise results: nine-point calibration, stirrer control, electrode test for pH glass electrodes, method memory, and RS232 interface.

In addition to pH measurement, the 781 pH/Ion Meter allows the determination of specific ions (e.g., Cl^- , F^- , NH_4^+) either by direct measurement or by fully automatic standard addition with a Dosimat.



856 Conductivity Module and 867 pH Module

Thanks to the five-ring measuring cells the new 856 Conductivity Module is ideal for measurements in drinking water according to DIN EN 27888 and EPA 120.1. The large range of linearity allows various types of water to be measured without recalibration. By combining the 856 Conductivity Module with the 867 pH Module it is even possible to measure the conductivity and pH value simultaneously in the same vessel.

Five-ring conductivity measuring cells

The main feature of the new five-ring measuring cells is their large range of linearity (0.005–100 mS/cm). This means it is possible to measure anything from drinking water to seawater without any calibration in between.

Water for pharmaceutical use (water for injection)

Conductivity

Particularly strict rules apply to the measurement of the conductivity of water for pharmaceutical use (water for injection) according to USP<645>. Apart from the highest level of precision, all the requirements of the U.S. FDA's 21 CFR Part 11 must be satisfied. The 856 Conductivity Module, together with the 900 Touch Control, PC Control, or **tiamo** (full or multi) guarantees this.

Conductivity measuring cell (stainless steel) with Pt 1000

This measuring cell was developed specifically for water samples with very low conductivity. The robust and easy to clean stainless-steel device is ideal for conductivity values <300 μ S/cm and thus for measuring water for pharmaceutical use.

pH value

The 867 pH Module provides all that is needed for measuring the pH value according to USP<791>. With 900 Touch Control, PC Control, or **tiamo** (full or multi), intelligent sensors and five-point calibration it meets the requirements of FDA 21 CFR Part 11. In conjunction with PC Control or 840 Touch Control it is possible to carry out an electrode test. Conductivity and pH value can be measured in the same vessel if the 856 Conductivity Module is combined with the 867 pH Module.



Titration

08

Carbonate hardness (temporary hardness, alkalinity, or acid binding capacity)

Temporary hardness is determined by endpoint titration with 0.1 mol/L HCl. The combined pH glass electrode Aquatrode plus was developed specifically for use in aqueous solutions. The rapidly responding membrane glass and the fixed ground-joint diaphragm ensure precise, low-noise measurements, and titration results with waters ranging from ultrapure to water with a high salt content.

Acid and base capacity according to DIN 38409-7

Acid and base capacity are parameters that describe the buffering capacity of water with respect to acids and bases. These are important sum parameters in water analysis, which characterize the pH stability of the sample. Both parameters are determined by titration to the pH values of 4.3 and 8.2. The former covers all alkaline parts by titration with hydrochloric acid, the latter all acidic parts by titration with caustic soda. Unlike standard pH electrodes, the Aquatrode plus has a special glass membrane that guarantees rapid, correct, and highly precise pH measurements and pH titrations in solutions that have a low ionic strength or are weakly buffered.

Calcium and magnesium according to DIN 38406-3 and EPA 130.2

With regard to the determination of water hardness, a distinction is made between temporary hardness (carbonate hardness) and permanent hardness (sulfate hardness). Another important parameter includes the total hardness that represents the sum of the dissolved alkaline earth metals, but that is approximated as the sum of the calcium and magnesium hardness. Temporary hardness is determined by end point titration with hydrochloric acid, total hardness by complexometric titration with Na₂EDTA as titrant, and a Ca²⁺-selective electrode.

The *tiamo* titration software allows third-party devices to be incorporated, for example, for turbidity measurements according to DIN EN ISO 7027, or for determining color according to DIN EN ISO 7887.

Chloride

Chloride ions are determined by potentiometric titration with AgNO₃ as titrant and a combined Ag-ring electrode, the Ag-Titrode, following prior pH adjustment with nitric acid. The maintenance-free Ag-Titrode uses a pH glass membrane as reference electrode, which means that no refilling of electrolyte is required.

Fluoride according to ASTM D3868 and sulfide according to ASTM D4658

Fluoride and sulfide ions are determined by ion-selective electrodes.

For fluoride determination, a buffer substance is added to the sample. This buffer substance both maintains the ionic strength, regulates the pH value and complexes interfering aluminum and iron(III) ions.

To measure sulfide, a buffer is added. This both regulates the pH value, and prevents the oxidation of sulfide by atmospheric oxygen.



Titration – Sum parameters

Sum parameters usually characterize similar chemical, physical, physicochemical or biological features of different components. Their advantage is in the fast determination and informative value, which allow the sample to be evaluated quickly. As an example, electrical conductivity provides valuable information on the salt content of a water sample. Another important sum parameter is the chemical oxidizability of water components, which provides indications of the type and quantity of organic material present in the sample.

According to the oxidizing power of the oxidizing agents used, a distinction is made between the permanganate index and the chemical oxygen demand (COD). While the permanganate index is the more informative parameter for samples with minimal or low contamination, COD is suitable for severely contaminated samples.

Permanganate index according to DIN EN ISO 8467

The permanganate index determines the easily oxidizable fraction of the organic constituents in water and is used, in a broader sense, to evaluate the organic chemical contamination in waters with minimal or low contamination, such as drinking water samples. For determination, the water sample is heated for ten minutes with sulfuric acid and an excess of permanganate solution of known concentration in a boiling water bath. After that, the permanganate consumption is determined by adding an excess of sodium oxalate solution and back-titrating the consumed oxalate with permanganate solution. The permanganate index is expressed as the quantity of oxygen in mg/L that would be needed for oxidation.

09



The MATi 13 (Metrohm Automated Titration) system for the fully automatic determination of the permanganate index



The MATi 12 system for fully automatic COD determination

Chemical oxygen demand according to DIN 38409-44 and ASTM D1252

The chemical oxygen demand (COD) is a measured value for the sum of the substances in a certain volume of water that can be oxidized by chromate. Chromate is a much stronger oxidizing agent than permanganate, which is why it also oxidizes most organic compounds practically completely into CO_2 . In sewage treatment plants, COD is regarded as a valuable indicator for evaluating treatment performance.

For volumetric determination of the COD, the sample of water is heated over a defined period with potassium

dichromate. The remaining quantity of potassium dichromate is then back-titrated with ammonium iron(II) sulfate.

The water constituents are oxidized either in a special COD heating device with reflux condensing or in a closed reaction vessel with an external heat source. Titration takes place directly in the reaction vessels without the need to transfer the content to other vessels. This prevents any sample losses and saves valuable time, especially when there is a high sample throughput.

Fully automated water analyzing system

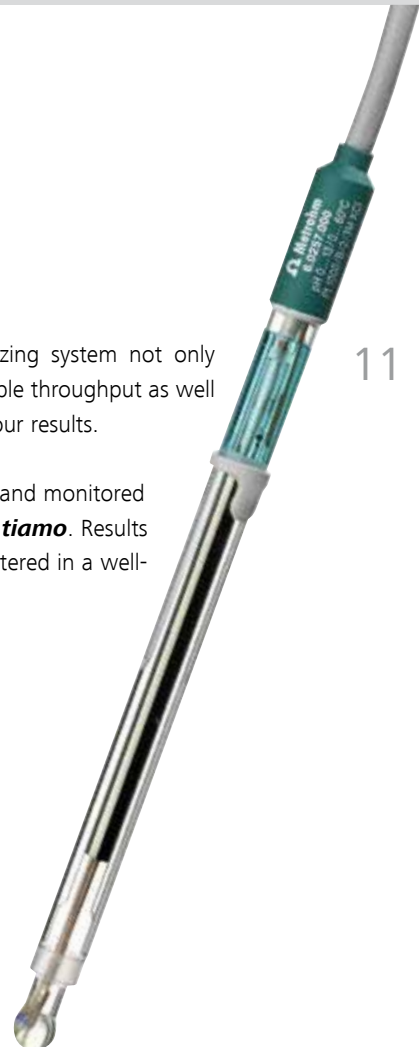
Comprehensive water analysis includes the determination of different sum parameters (e.g., conductivity, pH value, alkalinity, hardness) and several individual substances (e.g., ions). Frequently, these parameters – even in case of a high sample throughput – are sequentially determined on different instruments. This is very time consuming and requires repetitive sample preparations and expensive laboratory space. Why not save time and benefit from synergy effects by combining Metrohm devices in a single system that carries out all the mentioned analyses and sample preparations in a single run?

MATi 01 is just the answer to this question. The system is a customizable combination of the 815 Robotic USB Sample Processor XL, 905 Titrando, and 856 Conductivity Module. Apart from the determination of the aforementioned parameters, the system automatically performs the necessary sample preparation steps. This includes the metering of the sample as well as further liquid handling steps such as the accurate addition of titrant and auxiliary reagents. Up to 59 samples can be placed on the sample rack.

The fully automated water analyzing system not only saves time, but also increases sample throughput as well as precision and repeatability of your results.

All the devices are fully controlled and monitored by the powerful titration software **tiamo**. Results are centrally recorded and administered in a well-arranged database.

11



Aquatrode plus with Pt 1000



Fully automated water analysis with MATi 01

Ion chromatography

Modern ion chromatography (IC) allows efficient separation and determination of inorganic and low-molecular weight organic anions and cations. Various separation mechanisms and types of detection as well as the possibility of automation and sample preparation make IC a proven routine method in water and environmental analysis.

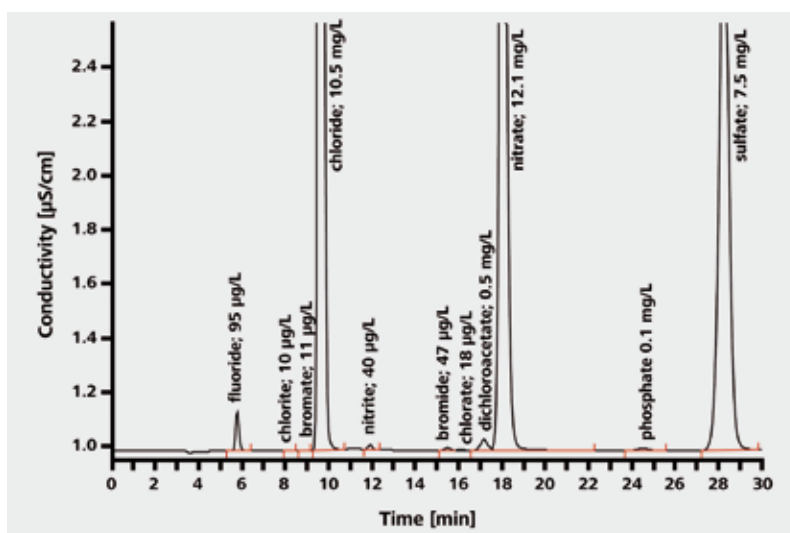
Drinking water and mineral water

Oxyhalides and standard anions according to EPA method 300.1

Chlorate, chlorite, and bromate are by-products that are

formed by oxidation of the halides when drinking water and mineral water are disinfected. Their concentration needs to be monitored on account of their suspected carcinogenic properties.

Prior to injection, the samples pass through the ultrafiltration cell mounted directly on the 858 Professional IC Sample Processor. Sample preparation and analysis are fully automatic. The equipment is controlled, the data collected and managed, and the system monitored by the intelligent MagIC Net chromatography software. The clear symbols, well laid-out presentation, and intuitive operation make analysis remarkably easy.



Drinking water sample, spiked with 10 µg/L of each ClO_2^- , BrO_3^- , ClO_3^- , 40 µg/L of each NO_2^- , Br^- , 100 µg/L PO_4^{3-} , 500 µg/L dichloroacetate; column: Metrosep A Supp 7 - 250/4.0; eluent: 3.6 mmol/L Na_2CO_3 , 0.8 mL/min; column temperature: 45 °C; sample volume: 20 µL; conductivity detection after sequential suppression





Bromate in drinking water

Because of the potentially carcinogenic properties of the bromate that can form during the ozonization of drinking water, this determination is very important. Depending on the required detection limit, different detection methods can be used. Conductivity detection with sequential

suppression allows the determination of bromate in the lower $\mu\text{g/L}$ range. In the ng/L range bromate can be detected by means of IC/MS coupling or post-column derivatization with potassium iodide and subsequent UV detection.

Bromate analysis: overview test methods and detection limits (acc. to DIN 32645)

	EPA method	Injection volume $[\mu\text{L}]$	Detection limit Ultrapure water $[\mu\text{g/L}]$	Detection limit Drinking water* $[\mu\text{g/L}]$
Conductivity detection with sequential suppression	300.1	100	0.130	0.390
IC/MS coupling; MS detection	—	100	0.006	0.007
Post-column derivatization with o-dianisidine; VIS detection	317.0	100	0.210	0.640
Post-column derivatization with KI; UV detection	326.0	1000	0.032	0.066

*Drinking water matrix: 100 mg/L of each chloride, sulfate, and carbonate



Ultrapure water

Anions and cations

Ultrapure water is used, for example, in the production of pharmaceuticals and semiconductors and as a central medium in thermal power plants. In the latter situation, it serves as the coolant, drives the turbines, and moderates nuclear fission. Determination of the substances in

the water is therefore of crucial importance. Anions and cations are important corrosion indicators and can be determined reliably down to trace concentrations (ng/L) after inline preconcentration, one of the applications of Metrohm Inline Sample Preparation (MISP).

Cation detection limits of the 940 Professional IC for direct injection and after preconcentration

	Detection limit					
	Lithium	Sodium	Ammonium	Potassium	Magnesium	Calcium
	[ng/L]					
Direct injection; 100 µL*	200	250	370	2700	2500	3800
Sample preconc. from 10 mL*	2	3	2	6	5	4

*Column: Metrosep C 3 - 250/4.0; eluent: 2.5 mmol/L HNO₃, 1 mL/min; column temperature: 40 °C; conductivity detection without suppression

Anion detection limits of the 940 Professional IC for direct injection and after preconcentration

	Detection limit						
	Fluoride	Chloride	Nitrite	Bromide	Nitrate	Phosphate	Sulfate
	[ng/L]						
Direct injection; 20 µL ¹	370	330	410	900	990	890	830
Sample preconc. from 10 mL ²	0.7	1.2	0.8	2.3	2.5	2.6	2.3

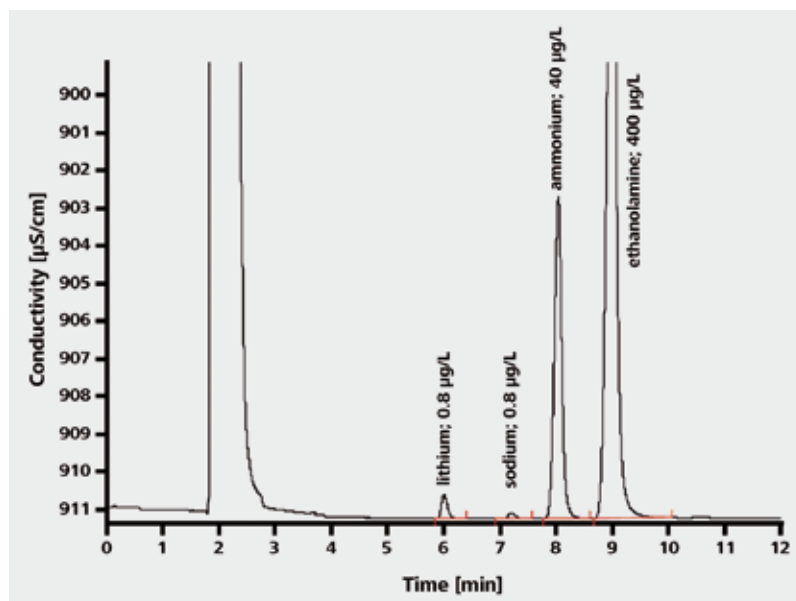
¹Column: Metrosep A Supp 5 - 100/4.0; eluent: 3.2 mmol/L Na₂CO₃, 1.0 mmol/L NaHCO₃, 0.7 mL/min; column temperature: 25 °C; conductivity detection after sequential suppression

²Column: Metrosep A Supp 7 - 250/4.0; eluent: 3.6 mmol/L Na₂CO₃, 0.8 mL/min; column temperature: 45 °C; conductivity detection after sequential suppression

The determination of cations in the secondary circuit of nuclear power plants is shown as an example. To prevent corrosion in the cooling circuit, the pH value is raised by adding Lewis bases such as, for example, ethanolamine and morpholine. Ion chromatographic determination of cations allows simultaneous, reliable determination of the amines, which means that IC can also be used to control the addition of amines.

940 Professional IC Vario with 800 Dosino (2x) and 815 Robotic USB Sample Processor XL





Spiked sample from the secondary circuit of a nuclear power plant; column: Metrosep C 4 - 250; Metrosep C PCC 1 HC for sample preconcentration; eluent: 2.5 mmol/L HNO_3 , 1.0 mL/min; column temperature: 45 °C; sample volume: 2.5 mL; conductivity detection without suppression



Voltammetry

16

Voltammetric trace and ultratrace analysis of drinking water, groundwater, surface water, seawater, and wastewater is used to determine electrochemically active inorganic ions. It is frequently employed to complement and validate spectroscopic methods. Its features are: compact equipment, relatively low investment and running costs, simple sample preparation, short analysis times, and high accuracy and sensitivity. In addition, unlike the spectroscopic methods, voltammetry is able to distinguish between different oxidation states of metal ions (speciation) as well as between free and bound metal ions. This provides important information regarding the bioavailability and toxicity of heavy metals. Voltammetry is especially suitable for laboratories in which only a few parameters have to be monitored with a moderate sample throughput. Important fields of application include envi-

ronmental monitoring, limnology, hydrography, oceanography, marine biology, and soil science.

884 Professional VA

The 884 Professional VA is a flexible measuring instrument for accurate and sensitive voltammetric analyses. The accompanying viva software enables individual optimization of methods.

909 UV Digester

With the 909 UV Digester, unwanted organics in surface water and wastewater samples can be digested quickly and safely, with no contamination. UV digestion is the ideal sample preparation for the voltammetric determination of heavy metals.

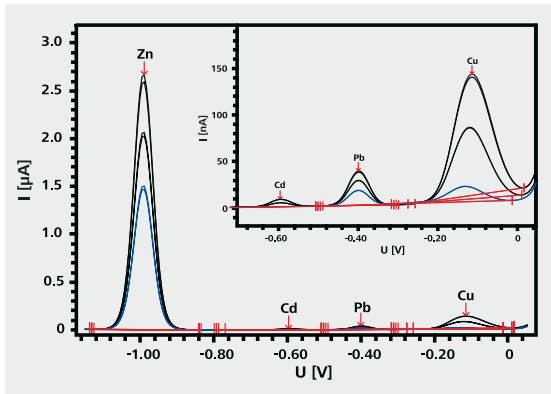


Drinking water and groundwater

Many toxic transition metals and a few anions can be determined voltammetrically, with a high degree of sensitivity and without prior sample preparation, in drinking water and groundwater. Here are a few relevant examples:

Zinc, cadmium, lead, copper, thallium, nickel, and cobalt

These metal ions must be determined regularly in water samples. DIN 38406 Part 16 describes the determination of these ions in different types of water.

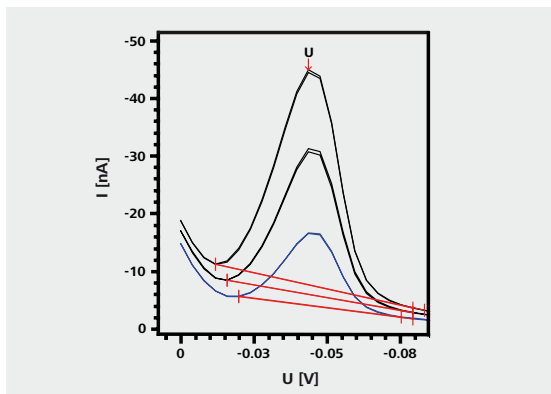


Voltammetric determination of zinc, cadmium, lead, and copper according to DIN 38406-16

Uranium

For adults, the World Health Organization (WHO) recommends a drinking water limit of 30 µg/L for uranium, which is radioactive and highly toxic. In Germany, the Drinking Water Directive only stipulates a limit of 10 µg/L.

With the 884 Professional VA dissolved uranium can be



Voltammogram of a uranium(VI) determination in a drinking water sample

determined easily and economically down to the ng/L range. By contrast, the spectroscopic analytical techniques are complicated and expensive.

Arsenic and mercury with the scTRACE Gold

Due to the toxicity of arsenic and mercury, the World Health Organization recommends a maximum content in the drinking water of 6 or 10 µg/L, respectively. Anodic stripping voltammetry using the scTRACE Gold offers a simple, low-cost alternative to spectroscopic determination for both elements.

The scTRACE Gold combines all three of the electrodes needed for the measurement. Selection of the measuring parameter makes it possible to distinguish between As(III) and As(V).

Moreover, inorganic mercury can also be determined with the scTRACE Gold. The detection limit in this case is 0.1 µg/L.

Element		Detection Limits [ng/L]
Antimony	Sb ^{III} /Sb ^V	200
Arsenic	As ^{III} /As ^V	100
Bismuth	Bi	500
Lead	Pb	50
Cadmium	Cd	50
Chromium	Cr ^{III} /Cr ^{VI}	25
Cobalt	Co	50
Iron	Fe ^{II} /Fe ^{III}	50
Copper	Cu	50
Molybdenum	Mo	50
Nickel	Ni	50
Platinum	Pt	0.1
Mercury	Hg	100
Rhodium	Rh	0.1
Selenium	Se ^{IV} /Se ^{VI}	300
Thallium	Tl	50
Uranium	U	25
Tungsten	W	200
Zinc	Zn	50

Seawater

Whereas the seawater salt matrix interferes with the determination of heavy metals in atomic spectrometric analysis, voltammetry allows direct determination without any sample preparation. Only the presence of organic compounds can affect voltammetric detection. By using the 909 UV Digester it is possible to remove the organic matrix quantitatively by UV photolysis within 60 minutes. With regard to use on research ships, the compactness and robustness of the 884 Professional VA are decisive advantages. Apart from its use to determine total metal concentration, voltammetry makes it possible to distinguish between the different oxidation states and also between free and bound metal ions.

Important applications in seawater analysis include the determination of a series of transition metals, some of them toxic, as illustrated by the following examples:

Determination of different chromium species

Chromium species differ considerably in their ecotoxicity: whereas Cr(III) is an important trace element for marine organisms, the strongly oxidizing chromium(VI) compounds are highly toxic.

Cadmium, lead, copper, and iron

Other important analytes are the elements cadmium, lead, and copper, which are usually determined on a mercury film electrode. Iron may be present in oxidation states II and III and is determined at the hanging mercury drop electrode (HMDE).

Wastewater

Voltammetric determination of many heavy metals is also possible in municipal or industrial wastewater. On account of the usually high organic load the sample is usually mineralized by means of UV digestion.



Cooling water and boiler feed water

All thermal power plants use water as the central medium for cooling and for generating steam. Only top-quality boiler water and cooling water can ensure efficient and trouble-free operation of the plant. Voltammetry allows the easy and rapid checking of important monitoring parameters such as copper, iron, zinc, cobalt, and manganese content.

Multiparameter analysis – titration, ion chromatography, and voltammetry

Fully automatic drinking water analyses

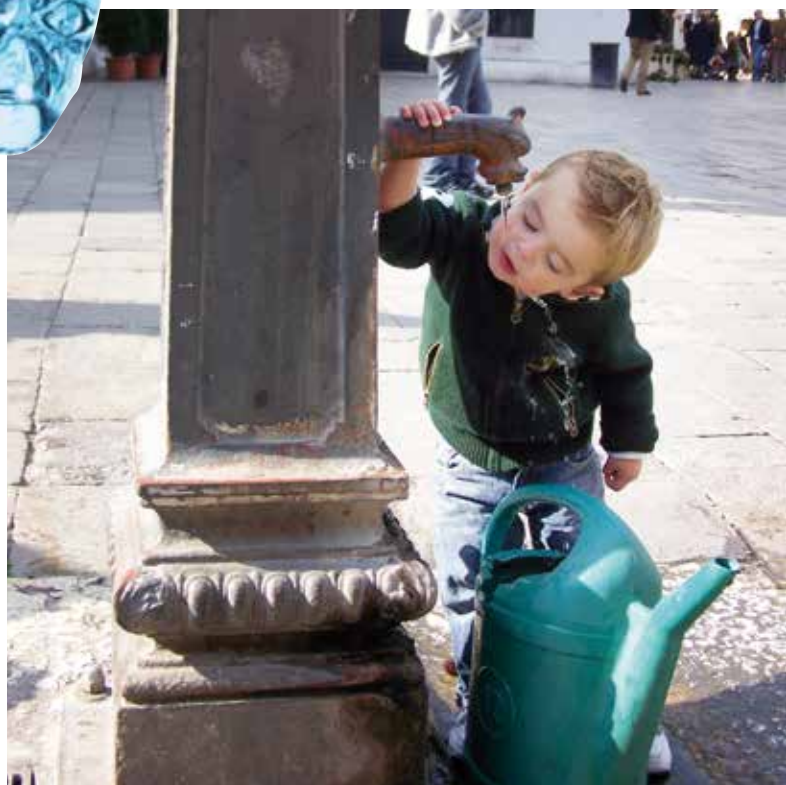
TitriC and VoltiC combine the advantages of direct measurement of pH value and conductivity, titration, ion chromatography, and voltammetry in single systems that provide fully automatic drinking water analyses. TitriC stands for the combination of direct measurement, titration, and ion chromatography – VoltiC for that of voltammetry and ion chromatography. All ionic components are determined reliably, quickly, and reproducibly. The

results are saved in the integral database and can be processed to produce a combined report.

Intelligent control and thoroughly tested technology guarantee reliable analyses regardless of the time of day or night. Up to one hundred samples can be analyzed fully automatically. This reduces the time required and increases the precision of the measurements.

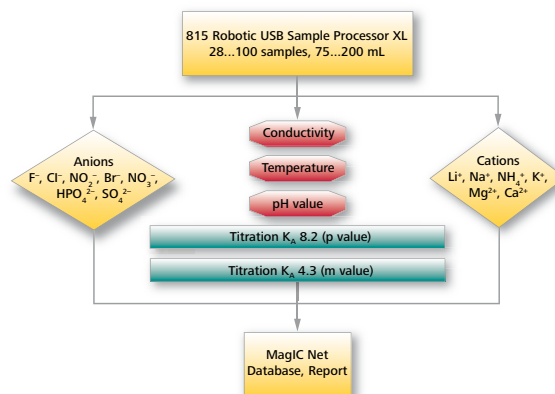
Minimal space requirements

Particular attention has been given to keeping space requirements to a minimum. The synergies between titration, direct measurement, ion chromatography, and voltammetry are also evident here. All methods use the same liquid handling units and a common sample changer. This helps to save both costs and space; a rapid return on investment is guaranteed.



TitriC is flexible

TitriC can be adapted to suit the particular analytical task. The application determines which parameters are of interest. Accordingly, different methods and procedures can be combined freely.



TitriC Vario pro II – Flowchart

TitriC determines the following parameters:

Direct measurements with TitriC

- pH value
- Temperature
- Conductivity

Titration with TitriC

- pH value (titration to pH = 8.2)
- m value (titration to pH = 4.3)
- Calcium
- Magnesium

Anion IC with TitriC

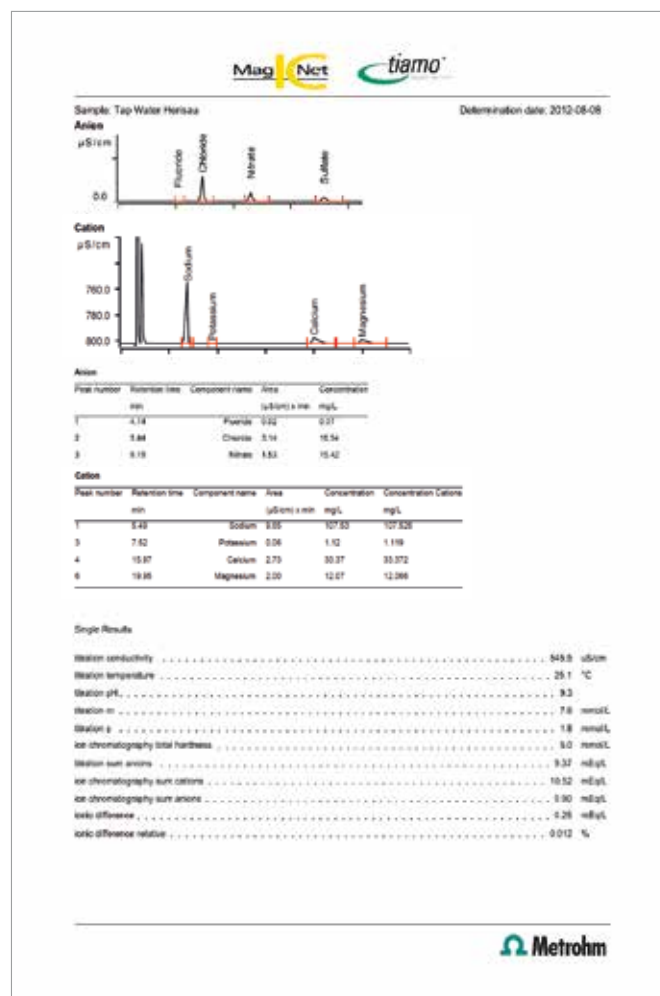
- Fluoride
- Chloride
- Bromide
- Nitrite
- Nitrate
- Phosphate
- Sulfate
- ...

Cation IC with TitriC

- Lithium
- Sodium
- Ammonium
- Potassium
- Calcium
- Magnesium
- ...

Calculations with TitriC

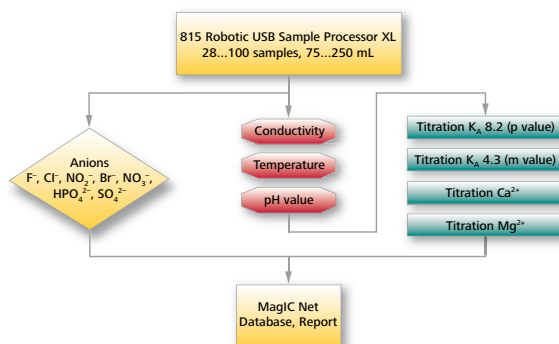
- Molar concentration of all cations
- Molar concentration of all anions
- Ionic balance
- Total water hardness
- ...



Report of a TitriC Vario pro system

TitriC Vario pro I – the basic system

Fully automatic system for direct measurement of temperature, conductivity, and pH value; the titrimetric determination of p value, m value, calcium and magnesium, and the determination of anions by ion chromatography.

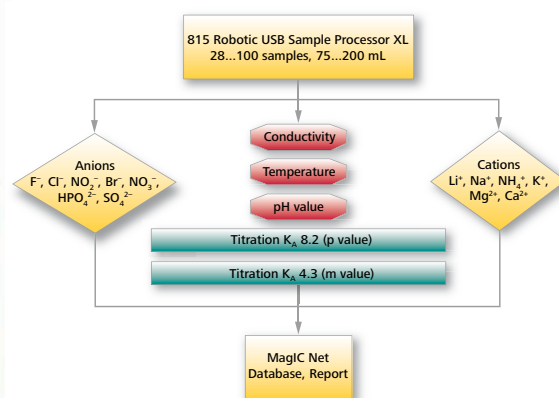


TitriC Vario pro I: The system consists of the 856 Conductivity Module, four 800 Dosinos, 802 Stirrer (rod stirrer), 905 Titrand, 815 Robotic USB Sample Processor XL and 930 Compact IC Flex with sequential suppression.

TitriC Vario pro II – for the complete determination of anions and cations

Fully automatic system for direct measurement of temperature, conductivity, and pH value, the titrimetric deter-

mination of p and m values, the determination of cations including calcium and magnesium, as well as anions by ion chromatography.

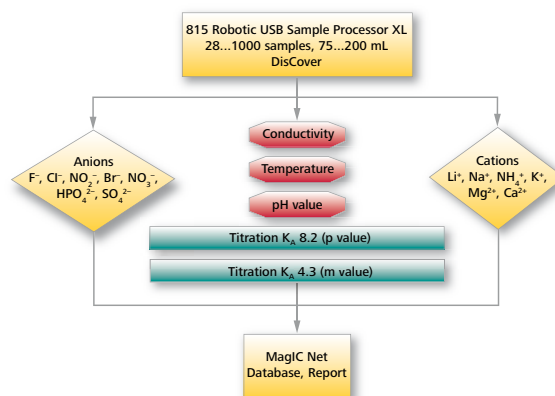


TitriC Vario pro II: The system consists of the 856 Conductivity Module, two 800 Dosinos, one 802 Stirrer, 905 Titrand, 815 Robotic USB Sample Processor XL, and two 930 Compact IC Flex.

TitriC Vario pro III – The professional solution with closed sample vessels

Fully automatic system for direct measurement of temperature, conductivity, and pH value, the titrimetric determination of p and m values, the determination of cations including calcium and magnesium, as well as

anions by ion chromatography. The sample changer is equipped with the DisCover function for automatic sample vessel cover removal.



TitriC Vario pro III: The system consists of the 856 Conductivity Module, two 800 Dosinos, 802 Stirrer (rod stirrer), 905 Titrand, 815 Robotic USB Sample Processor XL, and one 940 Professional IC for anions and cations.

VoltIC Vario pro I – The hyphenated IC and voltammetry system for parallel determination of anions, cations, and heavy metals

VoltIC Vario I is the perfect combination of IC and voltammetry for simultaneous determination of anions, cations, and heavy metals. MagIC Net controls IC instru-

ments, starts voltammetric determination, and summarizes the results from IC and voltammetry.



VoltIC Vario pro I: 940 Professional IC Vario for anion and cation analysis in combination with the 858 Professional Sample Processor and the 797 VA Computrace including Dosinos and Pump Station.

Atline process analysis

24

Frequently, water samples have to be analyzed rapidly to pick up changing process conditions. However, skilled laboratory staff is not always available around the clock and long distances to the laboratory often prevent fast sample analysis.

If, in such cases, the water sample can be analyzed directly on-site within the process, this is a decisive advantage. Metrohm ProcessLab, a robust and easy-to-use analysis system that is installed directly within the process, makes this possible. The sample is brought to the ProcessLab and the analysis is started with just one press of a button. ProcessLab is based on proven Metrohm components for titration and voltammetry. Its design is entirely modular; it is configured according to the analytical requirements and can be integrated ideally

into the process communication system through inputs and outputs (typically 4–20 mA). Just a few minutes after a sample has been taken, the relevant process information is available to a LIMS or the control room. The process conditions can be modified quickly and efficiently, if necessary. ProcessLab is therefore ideal for fast and independent process monitoring in the plant environment.

A ProcessLab analysis system consists of a TFT operating panel and an analysis module. For even easier and more comfortable operation, the operating panel is also available with touch function. With its splashproof housings, ProcessLab is ideally suited for use in harsh production environments.



ProcessLab analysis system with touch monitor and analysis module

Drinking water treatment

pH value, alkalinity, and active chlorine

These parameters are important variables in drinking water treatment. Processes such as deacidification, iron removal, flocculation, or disinfection are dependent on the pH value. Alkalinity is determined by the basic components present in the water, for example, carbonates and hydrogen carbonates. It defines the acid binding capacity or buffering capacity. Chlorine, by contrast, is used in water treatment plants as a disinfecting agent. If the concentration of chlorine is too low, the disinfecting effect is inadequate; if the concentration is too high, unwanted disinfection by-products form.

All three analytical parameters can be determined with ProcessLab and the results saved in a database. The measurements can be carried out quickly on-site, either centrally in the water treatment plant, or locally on the storage or high-level tank. Because of the simple integration of the system into the process, the analytical data and reports of off-limit conditions can be made available internally on the Intranet or in the control room, or externally on the Internet.



Cooling water and boiler feed water

pH value, conductivity, chloride, and total hardness

Cooling water and boiler feed water are used in thermal power plants, incinerators, and numerous industrial processes, including processes in the chemical industry. Once the pH value, conductivity, chloride concentration, and total hardness (Ca and Mg) have been determined, the key characteristics are known. In particular, cooling water and feed water with pH values below 7.0 or high chloride concentrations cause corrosion in the steel tanks and pipes. High total hardness leads to scale formation. All the parameters must remain below certain limits and can be determined reliably with ProcessLab.

Wastewater

Sample preparation – filtering of wastewater samples

Water samples often have to undergo sample preparation before analytical determination of their constituents. Sample preparation usually involves filtration or the addition of reagents. ProcessLab is able to perform many of these frequently repeated tasks automatically and can thereby considerably cut the time spent on routine analysis both in the production plant and in the laboratory.



Online process analysis

26

Customized online process control

Monitoring and control of water quality is of paramount importance. We use surface or groundwater for drinking water or for industrial purposes such as boiler feed, cooling water, or make-up water. Furthermore, strict controls on pollution require close control of surface and waste water derived from power plants or the chemical industry. Whatever the source of the water or whatever type of water is involved, Metrohm Process Analytics has the analyzer to monitor water quality and determine concentrations of relevant species in water.

Online analyzers from Metrohm Process Analytics run continuously 24 hours a day, 7 days a week without any operator intervention. Whether a single parameter in a single sample stream is involved or several different parameters in complex and multiple sample streams, Metrohm Process Analytics provides the right analyzer.

Proven wet chemistry methods

All analyzers are based on wet chemical analysis techniques such as titration, colorimetry, or ion-selective electrode measurements. Most of the well-established laboratory methods for water analysis can be easily transferred to the analyzers. In online analysis, sampling and sample preparation are at least as important as the analyzer itself. Metrohm Process Analytics has a lot of expertise in this area and configures custom-made sampling systems, for example, for filtration, sample taking from pressurized containers, or degassing.

Straightforward network integration

Analysis alone is of no use for water quality 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 the digital outputs. Digital inputs, in turn, can be used for remote start-stop purposes.

Single-Parameter online Analyzers

The ICON Analyzers and Alert Ion Analyzers are based on colorimetric and ion-selective electrode (ISE) methods, respectively. The ISE methods are generally used for measurements in the ppm and percent range, whereas the colorimetric techniques are used for the ppb to ppm range. Some typical applications:

Sodium and silica in power plants

Both sodium and silica play a major role in corrosion processes that occur in cooling water systems. For power plants, it is essential to monitor the concentrations of these species. With the Alert Ion Analyzer equipped with the Metrohm Na⁺ ISE, it is possible to measure sodium concentrations down to 1 ppb. If lower detection limits are required, the Alert Ion Analyzer can be replaced by the more accurate ICON Analyzer. Silica in cooling water or high-purity water can be determined with the ICON Colorimeter at concentrations as low as 1 ppb.



ICON Analyzer for silicate analysis in high-purity water



The ADI 2035 Process Analyzer comes in 3 basic configurations for potentiometric, photometric, and thermometric measurements.

Ammonia in drinking, waste or cooling water

As stated in a WHO report on drinking water: «The presence of elevated ammonia levels in raw water may interfere with the operation of manganese-removal filters because too much oxygen is consumed by nitrification, resulting in mouldy and earthy-tasting water. The presence of ammonia in raw water can lead to nitrate-rich drinking water due to catalytic oxidation or accidental colonization of filters by ammonia-oxidizing bacteria.»

The analysis of ammonia can be done either colorimetrically with an ICON Analyzer or with ion-selective electrodes using an Alert Ion Analyzer, depending on the required concentration range and detection limit. Manganese and nitrite can also be determined by both analyzers.

More demanding applications

For more complex determinations, multiple parameters or complex matrices such as surface water with high organic contents, Metrohm Process Analytics offers the ADI 201Y and ADI 204Y and the 2035 family of Process Analyzers. Typical applications for these analyzers are:

Hardness in drinking, industrial waste and surface water

This parameter is obtained by determining the calcium and magnesium concentration by complexometric titration with EDTA using a Cu^{2+} ISE. Depending on the desired concentration range and detection limit a Titrolyzer ADI 2016, a 2035 Process Analyzer configured for titration, or an ADI 2045TI Process Analyzer can be used.

Chemical oxygen demand (COD)

The COD sum parameter is commonly used to indirectly determine the amount of organic compounds in water.

The COD is measured in mg/L using a colorimetric method in which dichromate is added and the sample is digested. Depending on the concentration range an ADI 2019 or an ADI 2040 Process Analyzer is employed.

Total organic carbon content (TOC)

The total organic carbon content (TOC) is a highly important sum parameter that indicates all of the organic carbon in the sample examined. This value represents the level of organic contamination. As an online parameter, it can be readily automated and provides attractively high precision and accuracy. Another advantage: the determination requires no toxic chemicals.

The ADI 7010 TOC Analyzer is perfect for continuous monitoring of the TOC value in all types of water. The oxidation of organic carbon is accomplished using persulfate in the presence of UV light, and complies with EPA, ASTM, NAMUR and ISO regulations.



Metrohm Quality Service – Service you can rely on

Reliable results for the lifetime of your analytical instruments

Water analysis is a key component of analytical chemistry and covers the analysis of all water types, from ultrapure water and drinking water to wastewater. 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's global Quality Service, and regularly scheduled preventive maintenance in particular, extends your instrument's lifetime and ensures trouble-free operation. Maintenance work is carried out by qualified and certified service engineers. You have the option of selecting different types of service contracts depending on your

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

Metrohm Quality Service	Customer benefits
Metrohm Care Contracts	- Minimizes downtime through preventive maintenance - Cost control and savings through free or discounted replacement materials and consumables - Guaranteed reaction times and rapid on-site repair - Documented instrument certification as an ideal preparation for audits
Metrohm Software Care	High data security and maximum system performance through regular, professional software maintenance
Metrohm Compliance Service	- Customized services and documentation for analytical instrument qualification (AIQ) - Professional start-up (IQ/OQ or Certified Installation) and requalification or recertification by specifically trained employees
Metrohm Remote Support	Quick resolution of software and application issues directly at the workplace
Metrohm Dosing Test	- Calibration of burettes (e.g., dosing and exchange units) with certification - Accurate measurement results - Verification documentation for compliance with regulations and efficient audits
Metrohm Repair Service	- Rapid availability of repaired instruments thanks to decentralized repair workshops around the world and a central workshop at the manufacturer site - Highly qualified service technicians ensure sustainable repair success - Rapid resolution of problems and minimized downtimes through on-site emergency services and express repairs
Metrohm Spare Parts	- Original spare parts, made in Switzerland and available worldwide - Short delivery times through warehousing from local distributors - Investment security through ten-year spare parts guarantee after discontinuation
Metrohm Application Support	- Free access to the Metrohm Application Finder (www.metrohm.com/en/applications/) with more than 1800 applications (Application Bulletins, Application Notes, monographs, technical posters, and technical articles) - Rapid and professional resolution of any application issues through personal consultations with our specialists by e-mail, telephone, or remote support - Support for the solution of complex analytical problems, as well as method optimization on-site or at our application laboratories
Metrohm Training Programs	- Basic and advanced training with local representatives, at the Metrohm Academy or directly on-site - Efficient and proper use of all analytical methods, as well as results reliability through competently trained users - Training documentation and certificates for trouble-free audits

Ordering information

30

A water analysis overview is provided in the Metrohm monograph: «The determination of water constituents with Metrohm instruments», which can be downloaded and obtained free of charge from your local Metrohm supplier.

pH measurement, conductivity measurement, and titration

pH measurement

2.913.0110	913 pH Meter with Primatrode and accessories case
2.913.0210	913 pH Meter, laboratory version
2.780.0010	780 pH Meter including Unitrode
2.781.0010	781 pH/Ion Meter including Unitrode
2.867.0110	867 pH Module with Touch Control including iUnitrode
2.867.0210	867 pH Module with tiamo light and iUnitrode

Conductivity measurement

2.856.0110	856 Conductivity Module with Touch Control and five-ring conductivity measuring cell
2.856.0210	856 Conductivity Module with tiamo light and five-ring conductivity measuring cell
2.912.0210	912 Conductometer, laboratory version
2.912.0110	912 Conductometer with conductivity sensor and accessories case
2.914.0120	914 pH/Conductometer with Primatrode and accessories case
2.914.0220	914 pH/Conductometer, laboratory version
6.0915.100	Five-ring conductivity measuring cell $c = 0.7 \text{ cm}^{-1}$ with integrated Pt 1000 for 856 Conductivity Module
6.0915.130	Five-ring conductivity measuring cell $c = 1.0 \text{ cm}^{-1}$ with integrated Pt 1000 for 856 Conductivity Module
6.0916.040	Conductivity measuring cell (stainless steel) $c = 0.1 \text{ cm}^{-1}$ with Pt 1000 for 856 Conductivity Module
6.0917.080	Conductivity measuring cell, $c = 0.5 \text{ cm}^{-1}$ with Pt 1000 for 912/914
6.0918.040	Conductivity measuring cell made of stainless steel, $c = 0.1 \text{ cm}^{-1}$ with Pt 1000 for 912/914
6.0919.140	Conductivity measuring cell, $c = 1.6 \text{ cm}^{-1}$ with Pt 1000 for 912/914

Titration

2.905.0010	905 Titrand
MATi 01	Fully automated water analysis
MATi 12	Automated COD determination
MATi 13	Fully automated determination of the permanganate index in accordance with DIN EN ISO 8467
6.0253.100	Aquatrode plus
6.0257.600	LL-Aquatrode plus with Pt 1000
6.0277.300	iAquatrode plus with Pt 1000
6.0510.100	Combined Ca^{2+} -selective polymer membrane electrode
6.0502.150	F ⁻ -selective crystal membrane electrode
6.0430.100S	Ag Titrode with Ag_2S coating
6.0750.100	LL ISE Reference

Ion chromatography

Oxohalides plus standard anions

2.930.2560	930 Compact IC Flex Oven/SeS/PP/Deg
2.850.9010	IC Conductivity Detector
2.858.0020	858 Professional Sample Processor – Pump
6.2041.440	Sample rack 148 × 11 mL
6.5330.110	IC equipment: Inline ultrafiltration
6.1006.630	Metrosep A Supp 7 - 250/4.0
6.6059.311	MagIC Net 3.1 Compact



Anions and Cations in ultrapure water

2.940.2500	940 Professional IC Vario TWO/SeS/PP
2.850.9010	IC Conductivity Detector (2 ×)
2.815.0130	815 Robotic USB Sample Processor XL (2T/OP)
2.800.0010	800 Dosino (2 ×)
6.5330.140	IC equipment: MiPCT (2 ×)
6.9920.191	Sample rack 35 × 50 mL + 3 × 300 mL
6.1006.510	Metrosep A Supp 5 - 100/4.0
6.1050.430	Metrosep C 4 - 250/4.0
6.1006.310	Metrosep A PCC 1 HC/4.0
6.1010.310	Metrosep C PCC 1 HC/4.0
6.6059.312	MagIC Net 3.1 Professional

Suppressor rotors

6.2832.000	MSM Rotor A
6.2842.000	MSM-HC Rotor A
6.2844.000	MSM-LC Rotor A
6.2842.200	MSM-HC Rotor C
6.2842.020	Adapter sleeve for suppressor Vario to MSM and MSM-LC

Voltammetry

2.884.0110	884 Professional VA (MME)
2.884.1110	884 Professional VA semiautomated MME consisting of 884 Professional VA, measuring head for MME, and two 800 Dosinos.
MVA-22	Fully automated Professional VA system consisting of 884 Professional VA, measuring head for the MME, 919 IC Autosampler plus for VA, and two 800 Dosinos for automatic addition of auxiliary solutions. Allows the automatic processing of up to 28 samples. This system is the optimum solution for automatic analysis of small sample series.
	Required accessories
6.5339.030	VA Electrode Kit 884 MME
6.6065.202	viva 2.0 Full

TitriC and VoltiC systems

TitriC Vario pro I	The basic hyphenated system combining titration and IC
TitriC Vario pro II	The advanced hyphenated system combining titration and IC for complete ion analysis
TitriC Vario pro III	The high-end version combining titration and IC with closed sample vessels
VoltiC Vario pro I	The hyphenated IC and voltammetry system for parallel determination of ions and heavy metals

Process analysis

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

ADI 2045PL	ProcessLab system for atline determination of various parameters using titration, colorimetry, and ISE
ADI 201Y Series	Single method Process Analyzers, available with titration, colorimetry, or ISE
ADI 204Y Series	Multifunctional Process Analyzers, available with titration, ISE, colorimetry, and voltammetry
2035 Series	Analyzer family designed in 3 configurations: potentiometric, photometric, and thermometric titration
7010 TOC	Analyzer for determination of the total organic carbon content (TOC) in liquid samples
Furthermore, we offer the Plug and Analyze Series – ICON and Alert for single method, single component water analysis.	

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



water.metrohm.com