

# Water Analysis



Quality assurance of water



## Metrohm...

- is the global market leader in titration
- is the only company to offer a complete range of ion analysis equipment – titration, voltammetry and ion chromatography
- is a Swiss company and manufactures exclusively in Switzerland
- grants a 3-year instrument warranty and a 10-year warranty on chemical suppressors for ion chromatography
- provides you with unparalleled application expertise
- offers you more than 1300 applications free of charge
- supports you with expert service through local representatives and regional support centers
- is not listed on the stock exchange, but is owned by a foundation
- gives the interest of customers and employees priority over maximizing profit

## Metrohm – customized 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 ...

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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.

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>	Ultrapure water for pharmaceutical use	pH measurement	
Conductivity	DIN EN 27888	Drinking water	Conductivity measurement	7
	EPA 120.1	Acid rain Drinking water Seawater Wastewater	Conductivity measurement	
	USP <645>	Ultrapure water for pharmaceutical use	Conductivity measurement	
Total hardness Ca, Mg	EPA 130.2	Drinking water Wastewater	Titration	8
	EN ISO 9963	Drinking water Wastewater	Titration	
	DIN 38406-3	Drinking water Wastewater	Titration	
Alkalinity as CaCO <sub>3</sub>	EPA 310.1	Drinking water Seawater Wastewater	Titration	8
Cl <sup>-</sup>	DIN 38405-1	Drinking water Wastewater	Titration	8
Anions, e.g. F <sup>-</sup> , Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , etc.	EPA 300.1, Part A	Drinking water Wastewater	Ion chromatography	10
Oxyhalides	EPA 300.1, Part B	Drinking water Wastewater	Ion chromatography	10
	EPA 317.0	Drinking water	Ion chromatography	
	EPA 326.0	Drinking water	Ion chromatography	
	ASTM D 6581	Drinking water	Ion chromatography	
Cations, e.g. Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , etc.	ASTM D 6919	Drinking water Wastewater	Ion chromatography	12
	ISO 14911	Ultrapure water Wastewater	Ion chromatography	
pH value Conductivity Anions Cations	Various	All types of water	TitriC (Titration and Ion Chromatography)	14
Zn, Cd, Pb, Cu, Tl, Ni, Co	DIN 38406-16	Drinking water Wastewater	Voltammetry	18
U	DIN 38406-17	Drinking water Groundwater Raw water	Voltammetry	19
CN <sup>-</sup>	Sample preparation acc. to DIN 38405-13	Drinking water Wastewater	Voltammetry	19
Cd, Pb, Cu, Fe <sup>II</sup> /Fe <sup>III</sup> , Cr <sup>VI</sup>	–	Seawater	Voltammetry	20
Cu, Fe, Zn, Co	–	Boiler feed water Cooling water	Voltammetry	21
pH value, conductivity and parameters that can be determined by titration or voltammetry	Process-dependent specifications	Boiler feed water Cooling water Drinking water Process water Wastewater	Process analysis	22

## pH and conductivity measurement

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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. Whenever pH values are determined, Metrohm offers the ideal solution for every application.

### Drinking water

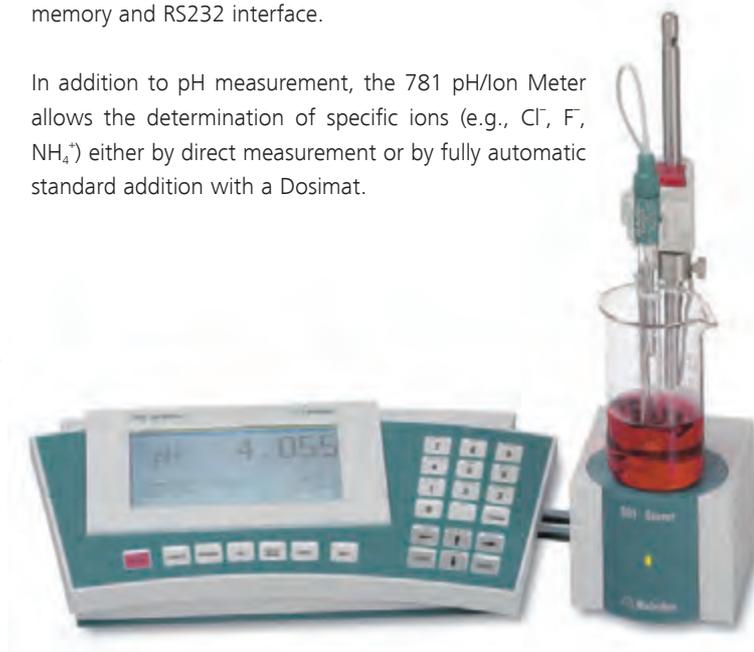
#### pH determination with 826 pH mobile and 827 pH lab

No matter whether you are carrying out routine pH measurements in the lab or moving from place to place – in neither case do you have to dispense with GLP: three-point calibration, automatic buffer recognition, temperature compensation, sample identification, GLP-compliant printout and a large memory for the measured values – all at an extremely attractive price.

#### 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.,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{NH}_4^+$ ) 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 840 Touch Control, PC Control or *tiamo*<sup>™</sup> (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  $\mu$ 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 840 Touch Control, PC Control or *tiamo*<sup>™</sup> (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

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## 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.

## Calcium and magnesium

Total hardness is determined by complexometric titration with Na<sub>2</sub>EDTA and a calcium-selective electrode. Depending on the concentration ratio between Ca and Mg, a direct distinction can be made between calcium hardness and magnesium hardness.

## Fluoride

Fluoride is determined with a fluoride-selective electrode. It is possible to choose between a direct potentiometric determination and the standard addition method.

## Chloride

Chloride ions are determined by means of potentiometric titration with AgNO<sub>3</sub> 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 there are no diaphragm problems and no refilling of electrolyte is required.

The *tiamo*<sup>TM</sup> 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.



809 Titrando – the allrounder

## 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 1 stands for **M**etrohm **A**utomated **T**itration system and is just the answer to this question. The system is a customizable combination of the 815 Robotic USB Sample Processor XL, 905 Titrande and 856 Conductivity Module. Apart from the determination of the mentioned 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*<sup>™</sup>. Results are centrally recorded and administered in a well-arranged database.

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Aquatrode plus with Pt 1000



Fully automated water analysis with MATi 1

## Ion chromatography

Modern ion chromatography (IC) allows efficient separation and determination of inorganic and low-molecular 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.

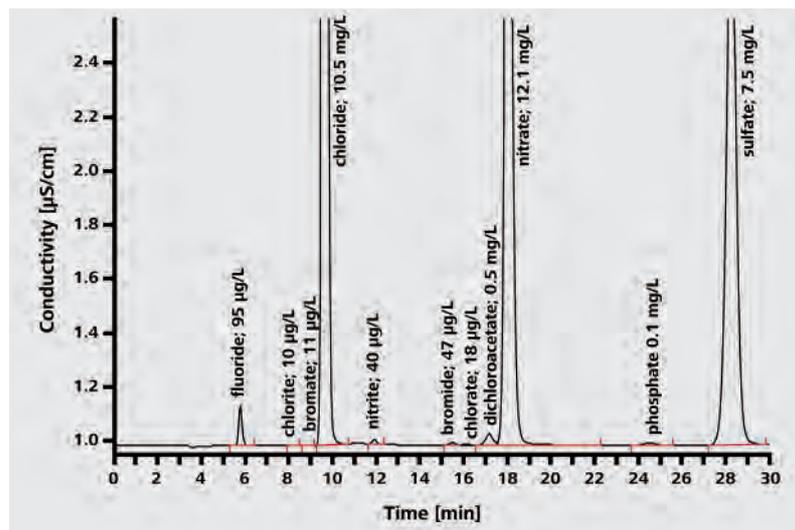
### Drinking water and mineral water

#### 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  $\text{ClO}_2^-$ ,  $\text{BrO}_3^-$ ,  $\text{ClO}_3^-$ , 40 µg/L of each  $\text{NO}_2^-$ ,  $\text{Br}^-$ , 100 µg/L  $\text{PO}_4^{3-}$ , 500 µg/L dichloroacetate; column: Metrosep A Supp 7 – 250 (6.1006.630); eluent: 3.6 mmol/L  $\text{Na}_2\text{CO}_3$ , 0.8 mL/min; column temperature: 45 °C; sample volume: 20 µL





### 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 chemical

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

### Overview of methods for bromate determination (acc. to DIN 32645), with detection limits

	EPA method	Injection volume [ $\mu\text{L}$ ]	Detection limit [ $\mu\text{g/L}$ ]	
			Ultrapure water	Drinking water*
Conductivity detection with chemical 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 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 850 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; eluent: 2.5 mmol/L HNO<sub>3</sub>, 1.0 mL/min; column temperature: 40 °C

### Anion detection limits of the 850 Professional IC for direct injection and after preconcentration

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

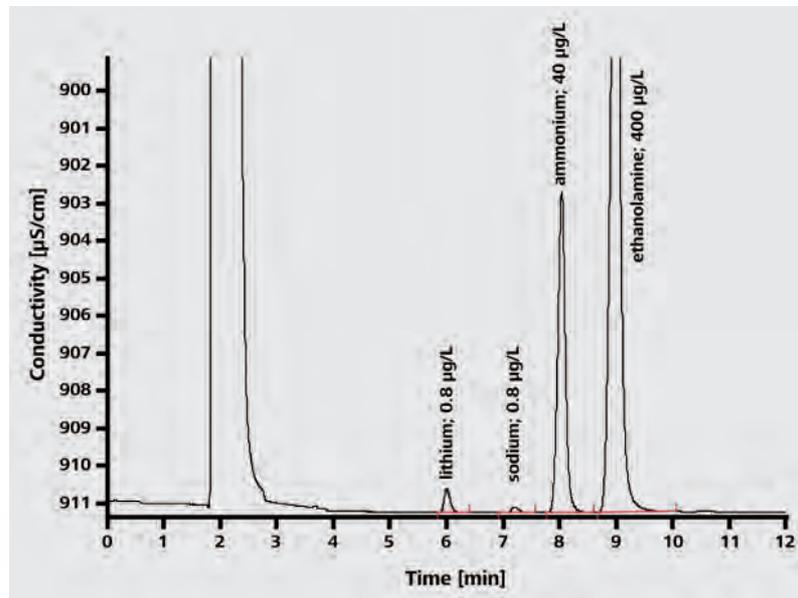
<sup>1</sup>Column: Metrosep A Supp 5 – 100; eluent: 3.2 mmol/L Na<sub>2</sub>CO<sub>3</sub>, 1.0 mmol/L NaHCO<sub>3</sub>, 0.7 mL/min; column temperature: 25 °C

<sup>2</sup>Column: Metrosep A Supp 7 – 250; eluent: 3.6 mmol/L Na<sub>2</sub>CO<sub>3</sub>, 0.8 mL/min; column temperature: 45 °C

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 without suppression allows simultaneous, reliable determination of the amines, which means that IC can also be used to control the addition of amines.



850 Professional IC with 800 Dosino and 858 Professional IC Sample Processor



Spiked sample from the secondary circuit of a nuclear power plant; column: Metrosep C 4 – 250 (6.1050.430); Metrosep C PCC 1 HC (6.1010.310) for sample pre-concentration; eluent: 2.5 mmol/L  $\text{HNO}_3$ , 1.0 mL/min; column temperature: 45 °C; sample volume: 2.5 mL



# TitriC – titration and ion chromatography

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## Fully automatic drinking water analyses

TitriC combines the advantages of direct measurement of pH value and conductivity, of titration and ion chromatography in a single system that provides fully automatic drinking water analyses. 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.

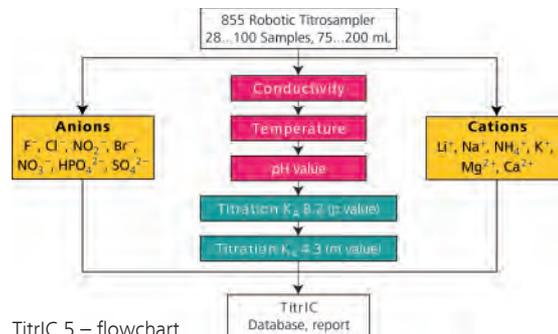
## Low space requirements

Particular attention has been given to keeping space requirements to a minimum. The synergies between titration, direct measurement and ion chromatography 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 5 – flowchart

### TitriC determines the following parameters:

#### Direct measurements with TitriC

- pH value
- Temperature
- Conductivity

#### Titration with TitriC

- p 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
- Total water hardness
- ...

#### Calculations with TitriC

- Molar concentration of all cations
- Molar concentration of all anions
- Ionic balance

TitriC-Report		Metrohm	
Printing date	2008-12-10	<b>IC data</b>	
<b>General data</b>		F [mg/L]	0.056
Sample ID	Drinking water Herisau	ClO2 [mg/L]	0
Date	2006-03-21	BrO3 [mg/L]	0
Time	23:44:54	Cl [mg/L]	13.065
Comment		NO2 [mg/L]	0.015
System comment	Within limit	Br [mg/L]	0.004
<b>Titration data</b>		ClO3 [mg/L]	0.003
pH	7.79	NO3 [mg/L]	10.11
Cond. [µS/cm]	587	PO4 [mg/L]	0.063
Temp. [°C]	22.26	SO4 [mg/L]	5.254
m value [mmol/L]	2.79	Na [mg/L]	6.138
p value [mmol/L]	0	NH4 [mg/L]	0
anions TIT	0	K [mg/L]	2.155
cations TIT	0	Mg [mg/L]	17.758
		Ca [mg/L]	83.913
		anions IC	6.02
		cations IC	5.971
		<b>Balances</b>	
		Sum anions [mEq/L]	6.02
		Sum cations [mEq/L]	5.971
		Ion balance [mEq/L]	-0.049
		Ion balance [%]	-0.41

TitriC report

TitriC 2.0 software combines the **tiamo™** and MagIC Net™ software packages. There are four versions of TitriC:

#### **TitriC 4 – the basic system**

Fully automatic system for the 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.



The system consists of the 856 Conductivity Module, four 800 Dosinos, 802 Stirrer (rod stirrer), 809 Titrand, 815 Robotic USB Sample Processor XL and 881 Compact IC pro with sequential suppression.

#### **TitriC 5 – for the complete determination of anions and cations**

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



The system consists of the 856 Conductivity Module, three 800 Dosinos, 802 Stirrer (rod stirrer), 855 Robotic Titrosampler, one 881 Compact IC pro without suppression for the determination of cations and one 881 Compact IC pro with sequential suppression for anion determination.

### TitriC 6 – the professional solution with sealed sample vessels

Fully automatic system for the direct measurement of temperature, conductivity and pH value; the titrimetric determination of p and m value; and the determination by ion chromatography of cations (including calcium and magnesium) and anions. The sample changer is equipped with the DisCover function for automatically removing the sample vessel covers.



The system consists of the 856 Conductivity Module, three 800 Dosinos, 802 Stirrer (rod stirrer), 809 Titrand, 815 Robotic USB Sample Processor XL and one 850 Professional IC for anions (sequential suppression) and cations.

### TitriC 7 – the solution for particle-containing samples

Fully automatic system for the direct measurement of temperature, conductivity and pH value; the titrimetric determination of p and m value; and the determination by ion chromatography of cations (including calcium and magnesium) and anions. Particle-containing samples have their particles removed by Metrohm Inline Ultrafiltration before determination by ion chromatography.



The system consists of the 856 Conductivity Module, two 800 Dosinos, 802 Stirrer (rod stirrer), 855 Robotic Titrator, one 850 Professional IC for anions with Sample Prep 2 and one 872 Extension Module IC Pump with an additional iDetector for cation determination.

# Voltammetry

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

## 797 VA Computrace

The 797 VA Computrace is a modern, user-friendly all-round measuring stand that enables accurate and sensitive determination of metal and non-metal traces with the help of voltammetric and polarographic methods.



## Detection limits

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



### 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

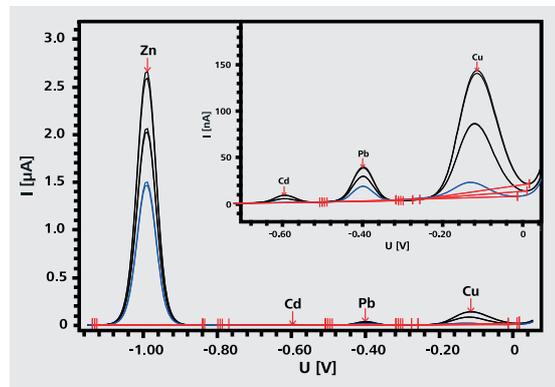
These metal ions must be determined regularly in water samples. DIN 38406 Part 16 describes the determination of these ions in different types of water.

#### Uranium

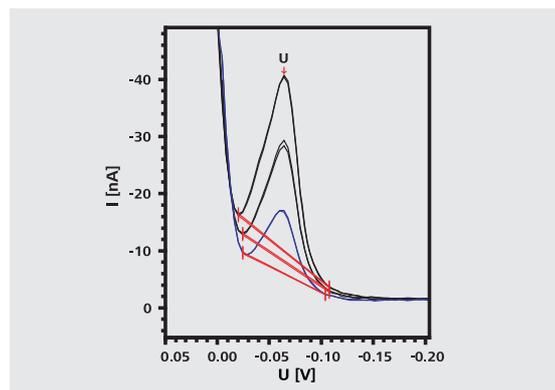
For adults the World Health Organization (WHO) recommends a drinking water limit of 15  $\mu\text{g/L}$  for uranium, which is radioactive and highly toxic. With the 797 VA Computrace, dissolved uranium can be determined easily and economically down to the  $\text{ng/L}$  range. By contrast, the spectroscopic analytical techniques are complicated and expensive.

#### Cyanide

Apart from heavy metals, voltammetry can also be used for trace analysis of a few anions. For example, free cyanide in a concentration range of 0.01...10  $\text{mg/L}$  can be determined easily and reliably even in sulfide-containing solutions with a large excess of phosphate, nitrate, sulfate and chloride.



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



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

### 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 705 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 797 VA Computrace 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.

## Atline process analysis

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Frequently water samples have to be analyzed rapidly to pick up changing process conditions. However, skilled laboratory staff is not always available round 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

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### 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 deriving from power plants or the chemical industry. Whatever the source of the water or whatever type of water is involved, Applikon Analytical has the analyzer to monitor water quality and determine concentrations of relevant species in water.

Online analyzers from Applikon Analytical 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, Applikon Analytical provides the right analyzer. The Alert analyzers have specifically been developed for water analysis and are easy to use and maintain.

### 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. Applikon Analytical 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.

### Alert range of analyzers

The Alert analyzers are either based on colorimetric or ion-selective electrode (ISE) methods. The ISE methods are generally used for measurements in the ppm and % range, whereas the colorimetric techniques are used for the ppb to ppm range. Some typical applications for the Alert analyzers are:

### 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<sup>+</sup> ISE, it is possible to measure sodium concentrations down to 1 ppb. If lower detection limits are required, the Alert analyzer can be replaced by the more accurate ADI 2018 analyzer. Silica in cooling water or high-purity water can be determined with the Alert Colorimeter at concentrations as low as 1 ppb.

Applikon Alert Ion analyzer for ammonia determination





ADI 2040 for COD determination

### 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.»

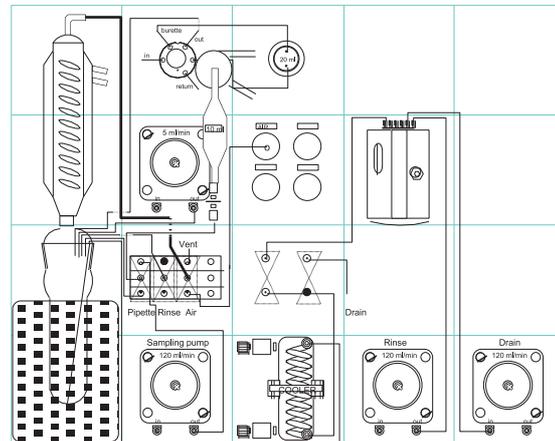
The analysis of ammonia with Alert analyzers can be done either colorimetrically or with ion-selective electrodes, depending on the required concentration range and detection limit. Manganese and the above-mentioned nitrite can also be determined by an Alert analyzer.

### More demanding applications

For more complex determinations, multiple parameters or complex matrices such as surface water with high organic contents, Applikon developed the ADI 201Y and ADI 2040 analyzers. Typical applications for these analyzers are:

### Hardness of drinking, industrial waste and surface water

This parameter is obtained by determining the calcium and magnesium concentration by complexometric titration with EDTA using a  $\text{Cu}^{2+}$  ISE. Depending on the desired concentration range and detection limit an ADI 2016 or ADI 2040 analyzer can be used.



Schematic representation of the colorimetric COD determination with the ADI 2040

### 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 is employed.



Applikon belongs to the Metrohm Group. The company produces online analytical instruments.

[www.applikon-analyzers.com](http://www.applikon-analyzers.com)



## Metrohm Quality Service®



### Security of results – for the lifetime of the analyzer

Throughout the world the name Metrohm stands for high-quality laboratory analyzers. They are designed to deliver high-precision results. Leading international companies with accurate water analysis as a core business also value Metrohm for our comprehensive services, which ensure that the responsible people in the laboratories can rely 100% on their analytical results throughout the entire lifetime of their Metrohm analytical instruments.

### Compliance with regulations

Metrohm Compliance Service® guarantees compliance with statutory requirements, irrespective of whether these are regulations of the U.S. Environmental Protection Agency (EPA), the U.S. Pharmacopeia or FDA 21 CFR Part 11. In order to obtain very precise and reliable analytical results right from the start with Metrohm analyzers, it makes sense to have instruments qualified and systems

validated by a Metrohm service expert. Metrohm offers qualification and validation documents as well as services, which fully meet the high requirements of industrial customers from regulated sectors.

These include:

- competent assistance with Design Qualification (DQ)
- documented installation and fast professional setup of new instruments with Installation Qualification (IQ)
- Operational Qualification (OQ), guaranteeing that Metrohm instruments meet the stated equipment specification. This ensures full performance capability.
- all qualification and validation work carried out solely by professionally trained and certified service technicians
- user training by experts
- efficient audit processes
- competent requalification and revalidation

### Metrohm Quality Service®

The worldwide Metrohm Quality Service®, especially the scheduled and preventive maintenance, extends the trouble-free life and operating time of your analysis systems. Qualified service technicians with proof of training carry out the maintenance work. You can choose bet-

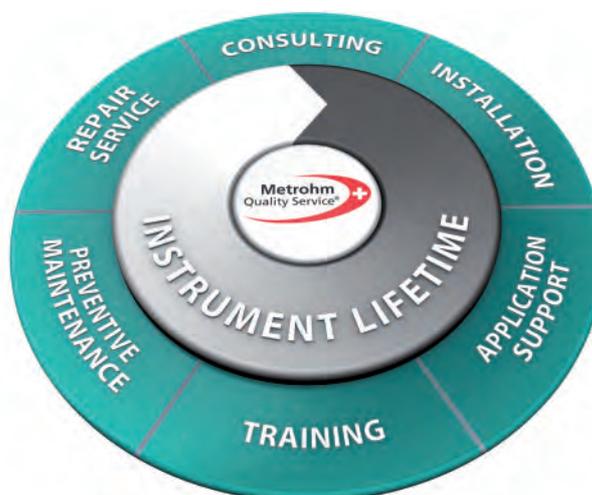
ween different types of service contracts. A full service contract, for example, offers you optimum security for work without any worries, whilst giving you complete control of costs and providing fully compliant documentation.

### Metrohm Quality Service® at a glance

Metrohm Quality Service®	Customer benefits
Application support by means of our vast selection of Application Bulletins, Application Notes, monographs, validation brochures, technical posters and articles Personal advice from our specialists by e-mail or telephone	Fast and professional solution to all arising application issues and complex analytical challenges
Training courses	Competent users contribute substantially to results Accurate results
Certified calibrations, e.g. of dosing and exchange units	Documentary evidence to comply with regulations and for efficient audits
Remote maintenance	Fast resolution of software issues
Back-up support	High data security
Emergency services, e.g. express repairs on-site	Short response time and thus rapid solution of problems and minimization of downtimes
Spare parts, made in Switzerland by Metrohm and available worldwide Guaranteed spare parts available for at least 10 years beyond instrument discontinuation date	Sustainable repair success, short delivery times, minimization of downtimes
Regional repair workshops available worldwide and a central workshop in Switzerland	Instruments soon available for reuse

Thanks to Metrohm Quality Service® you can rely on your results for the lifetime of the analytical instrument.

We look forward to working with you.



## Ordering information

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

### pH measurement, conductivity measurement and titration

#### pH measurement

2.826.0110	826 pH mobile with carrying case and Primatrode
2.827.0X1X	827 pH lab with Primatrode or Unitrode
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 and iUnitrode
2.867.0210	867 pH Module with <b>tiamo</b> <sup>TM</sup> 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 <b>tiamo</b> <sup>TM</sup> light and five-ring conductivity measuring cell
6.0915.100	Five-ring conductivity measuring cell $c = 0.7 \text{ cm}^{-1}$ with integrated Pt 1000
6.0915.130	Five-ring conductivity measuring cell $c = 1.0 \text{ cm}^{-1}$ with integrated Pt 1000
6.0916.040	Conductivity measuring cell (stainless steel) $c = 0.1 \text{ cm}^{-1}$ with Pt 1000

#### Titration

2.809.0010	809 Titrande
MATi1	Fully automated water analysis
6.0253.100	Aquatrode plus
6.0257.000	Aquatrode plus with Pt 1000
6.0277.300	iAquatrode plus with Pt 1000
6.0508.110	Ca <sup>2+</sup> -selective polymer membrane electrode
6.0502.150	F <sup>-</sup> -selective crystal membrane electrode
6.0430.100S	Ag Titrode with Ag <sub>2</sub> S coating
6.0750.100	LL ISE Reference

### Ion chromatography

#### Oxyhalides plus standard anions

2.881.0030	881 Compact IC pro – Anion – MCS
2.858.0020	858 Professional Sample Processor – Pump
6.2041.440	Sample rack 148 x 11 mL
6.1006.630	Metrosep A Supp 7 – 250
6.6059.111	MagIC Net <sup>TM</sup> 1.1 Compact

#### Options

6.5330.010	Equipment for ultrafiltration
6.2743.050	Sample tubes 11 mL (2000 pieces)
6.2743.070	PP stoppers with perforation for sealing sample tubes (2000 pieces)



### Cations in ultrapure water

2.850.1050	850 Professional IC Cation – Prep 2
2.858.0010	858 Professional Sample Processor
2.800.0010	800 Dosino
6.2841.100	Rinsing Station for IC Sample Processor
6.3032.210	Dosing Unit 10 mL
6.5330.040	IC equipment for liquid handling with Dosino
6.2041.390	Sample rack 16 x 120 mL
6.1014.200	Metrosep I Trap 1
6.1050.430	Metrosep C 4 – 250
6.1050.500	Metrosep C 4 Guard
6.1010.310	Metrosep C PCC 1 HC
6.6059.112	MagIC Net™ 1.1 Professional

### TitriC

TitriC 4	Basic system
TitriC 5	For the complete analysis of anions and cations
TitriC 6	For sealed sample vessels
TitriC 7	For samples containing particles

### Voltammetry

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

### Process analysis

875 ProcessLab is of modular design and consists of a complete Base Unit and any Extension Modules that may be required. The Base Unit contains all the necessary system components, but still requires to be completed by the wet-chemistry components mounted on the front panel and by I/O components.

2.875.0010	875 ProcessLab Base Unit, left-hinged door
2.875.0020	875 ProcessLab Base Unit, right-hinged door
2.875.0510	875 ProcessLab Base Unit with TFT operating panel incl. touch function, left-hinged door
2.875.0520	875 ProcessLab Base Unit with TFT operating panel incl. touch function, right-hinged door

Please contact your Metrohm supplier for further information. For a comprehensive documentation on Metrohm applications please consult [www.metrohm.com](http://www.metrohm.com)







[water.metrohm.com](http://water.metrohm.com)

