

# Environmental analysis



Quality control of water, soil, and air



## 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 analysis – 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 dependable on-site service worldwide
- is not listed on the stock exchange, but is owned by a foundation
- takes a sustainable approach to corporate management, putting the interests of customers and employees ahead of maximizing profit

# Metrohm – customized environmental analysis for water, soil, and air samples

## The importance of environmental analysis

The rapid growth in the world population has led to sharp increases in the consumption of energy and resources and in the production of consumer goods and chemicals. It is estimated that there are a total of 17 million chemical compounds on the market, including as many as 100,000 that are produced on a large industrial scale.

The effects of human activities on the environment are complex and call for sensitive analytical methods and powerful analytical instruments.

As a leading manufacturer of instruments for chemical analysis we know about these challenges. We offer you state-of-the-art instruments and systems, with which you can monitor the composition of your water, soil, and air samples.

## You can count on our know-how

Metrohm offers you complete solutions for very specific analytical issues. Your Metrohm contacts are professionals, who develop customized applications for you and provide you with professional support in all matters concerning environmental analysis.

Discover on the following pages the solutions Metrohm offers for analysis in the environmental compartments water, soil, and air.

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## Selected methods from the field of environmental analysis

Substances introduced into the environment are distributed among the environmental compartments water (hydrosphere), soil (pedosphere), rock (lithosphere), and air (atmosphere), as well as among the organisms living on them (biosphere). Only if we know the type and quantity of these contaminants can we protect the environment and its inhabitants. This requires internationally accepted standards, in which limits and test methods are defined. Metrohm instruments comply with numerous environmental standards. The following list contains a selection broken down according to environmental compartments.

### I. Water

As its physical state changes, water passes through all spheres. It is the most frequently analyzed environmental compartment and is also the easiest, because – unlike air or soil – it already exists in the liquid phase. If drinking water samples are to be analyzed, sample preparation is usually not necessary; however, it is usually unavoidable in the case of wastewater samples.

Parameter	Standard	Matrix	Method	Seite
Permanganate index	DIN EN ISO 8467	Drinking water, surface water	Titration	6
Chemical oxygen demand (COD)	ISO 6060 ISO 15705 ASTM D1252 DIN 38409-44	Drinking water, seawater, wastewater	Titration	7
Ca, Mg	ASTM D1126-12 EPA 130.2 DIN 38406-3 DIN 38409-6	Drinking water	Titration	8
Acid and base capacity	DIN 38409-7	All types of water	Titration	
Sulfide	ASTM D4658	All types of water	Titration	
Fluoride	ASTM D3868	Drinking water	Titration	
Free chlorine	EPA 340.2	Wastewater	Titration, Ion-selective electrode (ISE)	10
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.	ASTM D1253-12 EPA 330.1	All types of water	Titration	
Chromium(VI), Anions	DIN EN ISO 10304-1 EPA 300.0, Part A EPA 300.1, Part A EPA 9056A	All types of water Drinking and wastewater Drinking water Drinking water, wastewater	Ion chromatography	
Chromium(VI)	DIN EN ISO 10304-3	All types of water	Ion chromatography	
Oxyhalides	ASTM D5257 EPA 218.7	All types of water Wastewater	Ion chromatography	11
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.	DIN EN ISO 11206 ASTM D6581 DIN EN ISO 10304-4 DIN EN ISO 15061 EPA 300.0, Part B EPA 300.1, Part B EPA 317.0 EPA 326.0	Drinking water Drinking water All types of water Drinking and mineral water Drinking and wastewater Drinking water Drinking water Drinking water	Ion chromatography	
Amines (MMA, guanidine)	ISO 14911 ASTM D6919	Surface and drinking water Wastewater	Ion chromatography	
Bromate	–	Wastewater	Ion chromatography	
Bromate, halogenated acetic acids	EPA 321.8	Drinking water	Ion chromatography (IC-ICP/MS)	13
Perchlorate	EPA 557	Drinking water	Ion chromatography (IC-MS/MS)	
Hg, As, Cr	EPA 314.0 EPA 332.0	Drinking water	Ion chromatography	
Zn, Cd, Pb, Cu, Tl, Ni, Co	EPA 6800	Hydrosphere, biosphere	Ion chromatography (IC-ICP/MS)	
Cd, Pb, Cu, Fe <sup>II</sup> /Fe <sup>III</sup> , Cr <sup>VI</sup>	DIN 38406-16	Drinking water, wastewater	Voltammetry	15
CN <sup>-</sup>	–	Sea water	Voltammetry	
U	Sample preparation acc.to DIN 38405-13	Drinking water, wastewater	Voltammetry	
Anions, cations, heavy metals	DIN 38406-17	Groundwater, raw water drinking water	Voltammetry	
pH value, conductivity, anions, cations	Various	All types of water	VoltIC (Voltammetry and Ion chromatography)	16
pH value, conductivity, TOC, and parameters that can be determined by titration or voltammetry	Various	All types of water	TitriC (Titration and Ion chromatography)	17
	Process-dependent specifications	Drinking water, boiler feed water, cooling water, wastewater	Online and atline process analysis	19

Further standard-compliant methods for water analysis can be found in the brochure water analysis (8.000.5141EN).



## II. Soil

The soil is a multiphase system in which the hydrosphere, atmosphere, lithosphere, and biosphere exist side by side. It serves as a source of water and nutrients for plants, is a habitat for a large number of organisms, and is an important carbon sink. Harmful soil pollutants can easily

enter the human body through ingestion of animal and plant matter. The constituents of soil are very difficult to access and difficult to mobilize. Sample preparation usually involves extraction and digestion procedures.

Parameter	Standard	Matrix	Method	Seite
pH value	ISO 10390	Soil	pH measurement	22
Conductivity	ISO 11265	Soil	Conductivity measurement	23
Total organic carbon (TOC)	–	Soil	Titration	24
Cyanide	ISO 11262	Soil	Continuous flow analysis	25
Anions, e.g., F <sup>-</sup> , Cl <sup>-</sup>	–	Soil	Titration	
Anions	EPA Method 9056	Solid waste	Ion chromatography	
Perchlorate	EPA Method 6860	Soil Solid waste	Ion chromatography	
Chromium(VI)	ISO 15192 DIN EN 15192 EPA 3060A EPA 7199	Soil	Ion chromatography	26
Anions and cations	–	Soil	Ion chromatography	27
Trace elements	DIN ISO 11466 DIN ISO 19730	Soil	Voltammetry	28
Organophosphorus pesticide residues	AOAC 970.53	Soil	Voltammetry	

## III. Air

The atmosphere is an important thermal buffer against space, and protects the earth from cosmic radiation. It is the place where clouds are formed and water is present there in all its physical states. Thus it is a heterogeneous mixture of finely dispersed, solid or liquid particles in a gas (air). Its constituents are characterized by extreme

mobility, enter our bodies easily through breathing, and influence the climate and weather. Filter methods, and aerosol and gas collectors bring the constituents of air into the aqueous phase, which is preferable for chemical analysis.

Parameter	Standard	Matrix	Method	Seite
Saccharidic tracers	–	Particulate matter	Ion chromatography, filter	31
Chromium(VI)	ISO 16740 ASTM D6832 ASTM D7614-12	Workplace air	Ion chromatography, filter	32
Pb, Cd, Zn, Cu	–	Particulate matter	Voltammetry, filter	33
Anions and cations	–	Particulate matter	Ion chromatography, PILS*	35
Pb, Cd, Zn, Cu	–	Particulate matter	Voltammetry, PILS*	
Anions, cations, Pb, Cd, Zn, Cu	–	Particulate matter	Ion chromatography and voltammetry, PILS*	36
Hydrogen chloride	DIN EN 14791	Emissions, chimneys	Ion chromatography, MARGA*	38
Sulfur dioxide	DIN EN 14791	Emissions, chimneys	Ion chromatography, MARGA*	
Nitrogen dioxide	DIN EN 16339	Ambient air	Ion chromatography, MARGA*	

\* PILS is a semicontinuous aerosol sampler that is coupled to one or two analyzers (e.g., IC and/or VA); MARGA is the combination of aerosol and gas sampler including ion chromatographs.



## I. Water

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### Titration

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. Thus, for 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.



The MATi 13 system for 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  $\text{CO}_2$ . 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.

#### Automation solutions from Metrohm

Manual determination of the permanganate index and COD involves a great deal of work and, because the individual manual steps are difficult to reproduce, usually means inaccurate results.

Metrohm solves this problem with a fully automated system in which **tiamo** titration software controls all the individual steps – from sample preparation and the addition of the various solutions right through to the recording and archiving of data. Identical sequences guarantee unique reproducibility. New applications can be added to the freely configurable systems at any time, no matter whether they are for the determination of the pH value, conductivity, acid capacity, or for coupling with an ion chromatograph. Thus, it is possible to adapt any standard system individually to the particular task in the laboratory.



### 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 endpoint titration with hydrochloric acid, and total hardness by complexometric titration with  $\text{Na}_2\text{EDTA}$  as titrant and a  $\text{Ca}^{2+}$ -selective electrode.

### Chloride

Chloride ions are determined by potentiometric titration with  $\text{AgNO}_3$  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.



Combined polymer membrane electrode for calcium and magnesium determination



Ag-Titrode for chloride determination



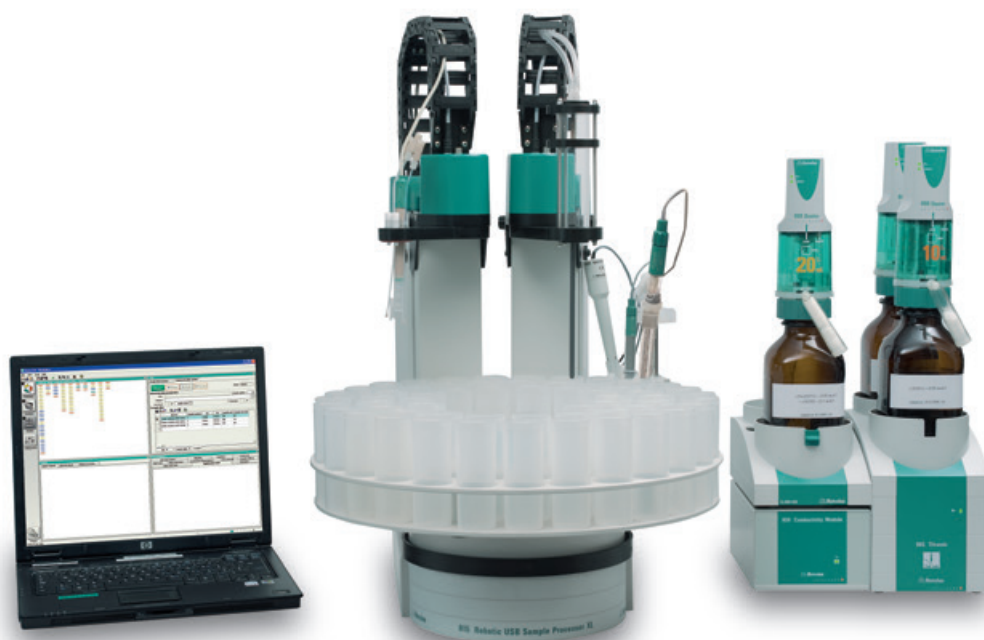
Ion-selective electrode, F



### Automation – efficient and more reproducible

The MATi 01 is an excellent example of how our system solutions simplify your everyday laboratory work, whether it be sample preparation, conductivity and pH measurements, or the fully automatic determination of alkalinity and water hardness in a single run from a prepared sample beaker. Gone are the days when a different instrument was required for each parameter, after which the data had to be transferred tediously by hand into the LIMS. In addition

to the time savings, more reproducible results can be achieved through automation, especially when many samples are involved, and particularly in shift operations. But that is not all: the **tiamo** titration software also allows numerous third-party devices to be incorporated – for example, for determining turbidity according to DIN EN ISO 7027 or for determining color according to DIN EN ISO 7887.



The MATi 01 system for fully automatic water analysis, including sample measurement

## Ion chromatography

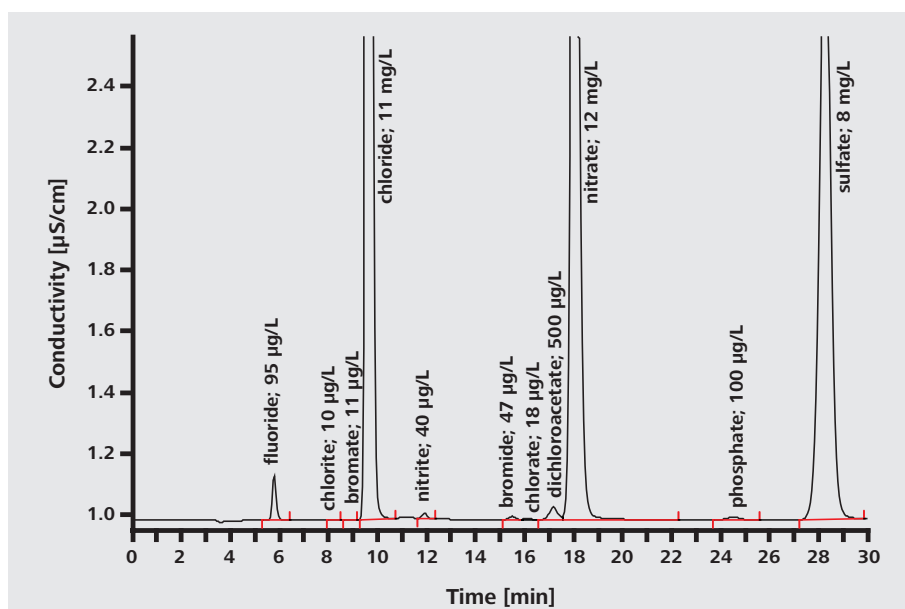
Modern ion chromatography (IC) allows efficient separation and determination of inorganic and low-molecular organic anions and cations. Various separation mechanisms and types of detection as well as the possibility of automated sample preparation make IC a proven routine method in water and environmental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

### Oxyhalides and standard anions in drinking water (EPA 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 concentrations need

to be monitored on account of their suspected carcinogenic properties.

Before injection, the samples pass through the ultrafiltration cell mounted directly on the 858 Professional 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 - 250/4.0; eluent: 3.6 mmol/L  $\text{Na}_2\text{CO}_3$ , 0.8 mL/min; column temperature: 45 °C; sample volume: 20 µL; conductivity detection after sequential suppression.

940 Professional IC Vario with 941 Eluent Production Module and 858 Professional Sample Processor for the fully automated anion and cation analysis in drinking water.

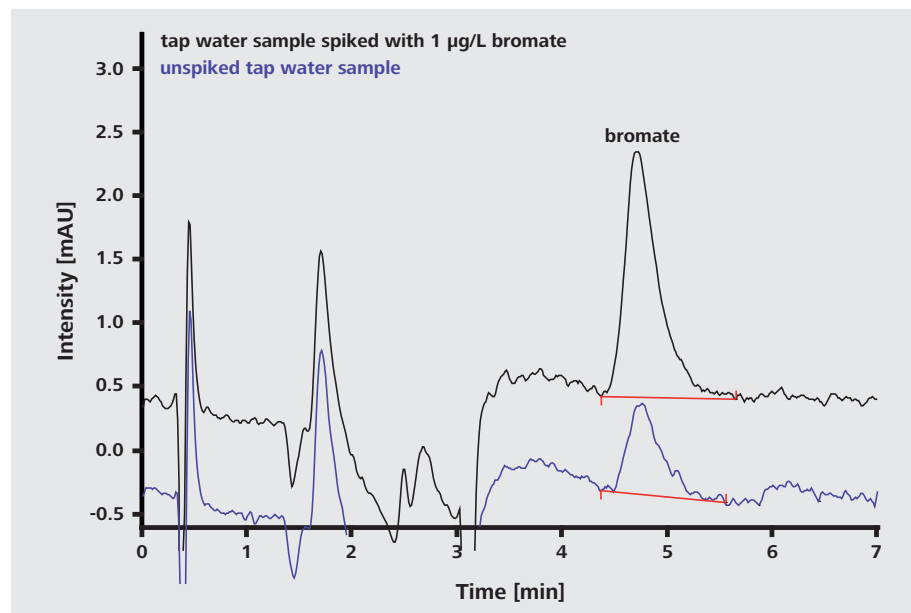




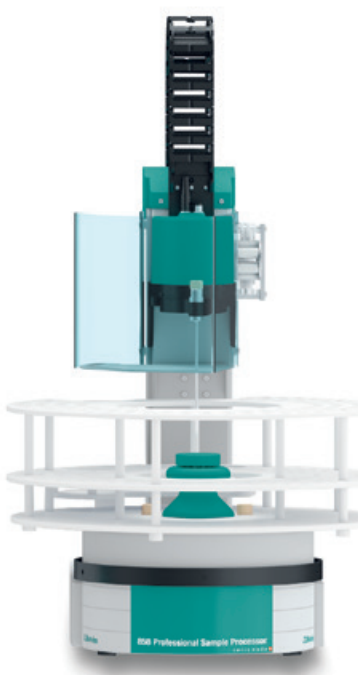
### Bromate in drinking water (EPA 326.0)

Bromate forms during the ozonization of drinking water. Several international standards stipulate detection limits and test methods. 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  $\text{ng/L}$  range bromate can be detected by means of IC/MS coupling or post-column derivatization with potassium iodide and subsequent UV detection.



Spiked and unspiked drinking water sample; column: Metrosep A Supp 16 - 100/4.0; eluent: 100 mmol/L  $\text{H}_2\text{SO}_4$ , 19.3  $\mu\text{mol/L}$  ammonium molybdate tetrahydrate, 0.8 mL/min; post-column reagent: 0.27 mol/L KI, flow rate: 0.2 mL/min; column temperature: 45 °C; UV detection, wavelength: 352 nm; sample volume: 1000  $\mu\text{L}$



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

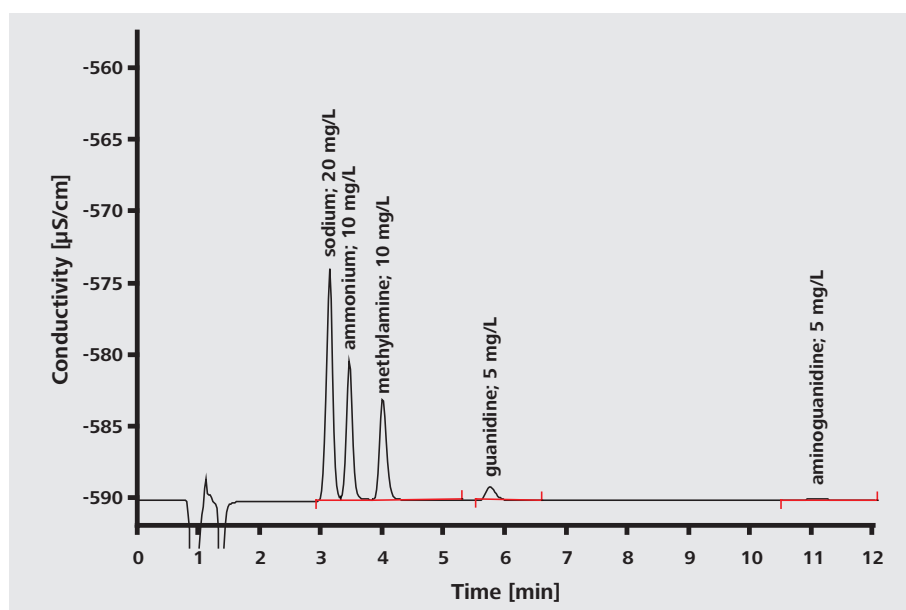
	EPA method	Injection volume [ $\mu\text{L}$ ]	Detection limit Ultrapure water [ $\mu\text{g/L}$ ]	Detection limit Drinking water* [ $\mu\text{g/L}$ ]
Conductivity detection with sequential suppression	300.1	100	0.130	0.390
IC/MS coupling; MS detection	—	100	0.006	0.007
Post-column derivatization with 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

### Aliphatic amines in wastewater

Aliphatic amines are important starting materials and intermediate products in the chemical and pharmaceutical industries. They are used to produce solvents, crop protection agents, polymers, detergents, dyes, explosives, lubricants, and pharmaceuticals. Their use on a large industrial scale has led to significant discharges into aquatic systems. Secondary amines, especially, are regarded as hazardous to waters, as they react even at trace concentrations with nitrite to form carcinogenic nitrosamines.

Short-chain aliphatic amines in industrial wastewaters can be determined easily on a cation-exchange column with subsequent conductivity detection. Not only important amines (methylamine, dimethylamine, trimethylamine, ethanolamines, guanidine, etc.), but also alkali metals and alkaline earth metals can be detected in a single determination. There is no need for complicated derivatization procedures, such as those in gas chromatography. Interfering particles, colloids, algae, or bacteria present in many (waste)water samples are removed fully automatically by Inline Ultrafiltration before analysis.



Water sample spiked with wastewater-typical amines; column: Metrosep C 4 - 100/4.0; eluent: 1.7 mmol/L  $\text{HNO}_3$ , 0.7 mmol/L dipicolinic acid, 5% acetone, 0.9 mL/min; sample volume: 10  $\mu\text{L}$ ; non-suppressed conductivity detection

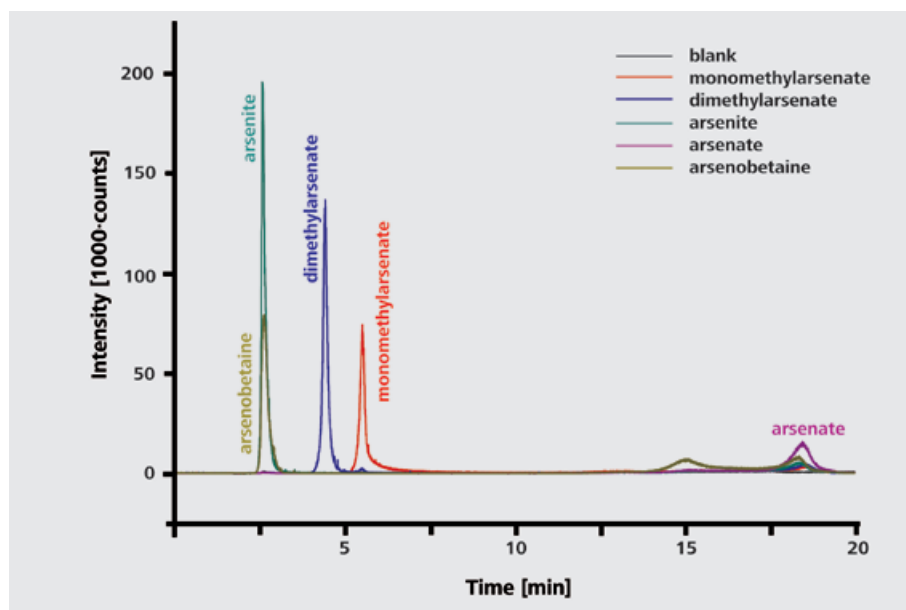


Cation analysis after Inline Ultrafiltration using 930 Compact IC Flex with 919 IC Autosampler plus

### Modern detection methods in IC

Coupling IC with mass spectrometry (MS) and inductively coupled plasma mass spectrometry (ICP/MS) brings detection limits down to ultratrace levels. Whereas the great advantage of structure-specific IC/MS is that it is possible to identify compounds not only by way of their retention time but also on the basis of their MS spectrum (organic acids), IC-ICP/MS enables a distinction to be

made between the different oxidation states of one and the same element. This element species analysis is important for elements such as arsenic, chromium, mercury, selenium, and gadolinium, which occur as simple elemental and molecular ions or as polar and ionic coordination compounds, and display different toxicities, depending on their bonding.



Separation and detection of arsenite, monomethylarsenate, dimethylarsenate, and arsenate by IC-ICP/MS; column: Metrosep A Supp 15 - 150/4.0; eluent: 8 mmol/L ammonium nitrate, pH = 8.3, 0.7 mL/min; sample volume: 10  $\mu$ L; ICP/MS: without reaction and collision mode, m/z: 75

### Further applications

Analyte	Coupling	EPA method	Remark
Bromate	IC/MS	–	along with other oxyhalides
	IC-MS/MS	EPA 557	along with haloacetic acids and dalapon
	IC-ICP/MS	EPA 321.8	after removal of haloacetic acids
Perchlorate	IC/MS	EPA 332.0 EPA 6860	in water and soil samples
Anions and organic acids	IC/MS	–	parallel determination in various matrices
Cations	IC/MS	–	alkali and alkaline earth metals as well as transition metals
Amines	IC/MS	–	very sensitive determination in water and food samples
Organic acids	IC/MS	–	in process water along with a high salt matrix
Carbohydrates	IC/MS	–	for peak confirmation after quantitative analysis using pulsed amperometric detection
Chromium	IC-ICP/MS	EPA 6800	speciation analysis
Arsenic	IC-ICP/MS	–	speciation analysis
Selenium	IC-ICP/MS	EPA 6800	speciation analysis
Mercury	IC-ICP/MS	EPA 6800	isotope dilution mass spectrometry
Gadolinium-containing MRI contrast agents	IC-ICP/MS	–	analysis of gadolinium chelates (Gadovist, Magnevist, etc.) and free gadolinium ions



## Voltammetry

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.

### Speciation analysis

Another advantage of voltammetry is the possibility 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.

### Determination of the complexation capacity

Natural waters often contain dissolved organic compounds that complex heavy metals and thus change bioavailability and toxicity of the latter. The parameter used to quantify the organic ligands in a sample is the complexation capacity; it indicates the amount of heavy metal ions which are barely complexed. Determination is performed by voltammetric titration. After each addition of

metal titrant, a voltammogram is registered. Plotting the currents of the respective peak heights versus the metal concentration provides a titration curve from which the complexation capacity is deduced.

### Versatile application areas

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.

### 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

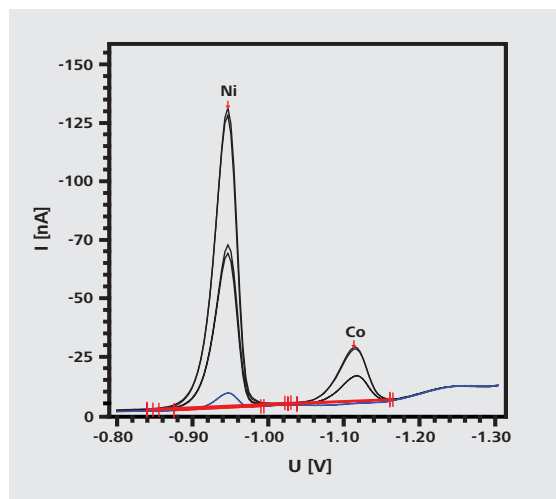
With the 909 UV Digester, unwanted organics in surface water and wastewater samples can be digested quickly and safely, with no contamination. UV digestion is the ideal sample preparation for the voltammetric determination of heavy metals.



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:

#### 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 nickel and cobalt in seawater according to DIN 38406-16

#### 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 determina-

tion 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.

#### 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	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



The fully automatic VoltIC Vario pro consists of several 800 Dosinos, a 797 VA Computrace, an 858 Professional Sample Processor, and a 940 Professional IC Vario (from right to left).

## VoltIC Vario pro – Voltammetry and Ion Chromatography

VoltIC Vario pro combines voltammetry (VA) and ion chromatography (IC) in a single system and permits the fully automatic analysis of anions, cations, and heavy metals. The necessary sample preparation steps are performed by sharing the same liquid handling system and sample changer, which directs the samples to the VA analyzer and the ion chromatographs. VoltIC Vario pro can be controlled with just one software. All the results are filed in a single database and can be converted into an easily readable report by pressing a button.

VoltIC Vario pro is very flexible and can be easily adapted to a wide variety of requirements in the analytical laboratory. Available Metrohm instruments (IC and VA) can be easily extended to a «VoltIC Vario pro» system.

Results				
Anions				
Component name	Retention time [min]	Height [μS/cm]	Area [(μS/cm) × min]	Concentration [ppb]
Fluoride	4.11	0.060	0.009	46.826
Chloride	6.03	17.081	3.365	6668.838
Bromide	8.92	0.004	0.001	8.271
Nitrate	10.01	5.025	1.158	6816.264
Sulfate	16.38	2.036	0.711	8341.677
Cations				
Component name	Retention time [min]	Height [μS/cm]	Area [(μS/cm) × min]	Concentration [ppb]
Sodium	3.74	6.629	0.765	6323.031
Potassium	5.49	0.551	0.093	1493.994
Calcium	10.59	9.780	7.772	77385.319
Magnesium	13.81	5.060	4.019	19096.590
Single results				
Analysis - ID: 1206131144_dth				
Cadmium by VA: n.d. μg/L				
Copper by VA: 17.029 μg/L				
Lead by VA: 0.287 μg/L				
Zinc by VA: 75.464 μg/L				

The VoltIC Vario pro Report: All the results at a glance



## TitriC Vario pro – Titration and Ion Chromatography

TitriC Vario pro stands for a unique combination of direct measurement, titration, and ion chromatography and permits the fully automatic determination of temperature, conductivity, pH as well as p and m value, alkalinity, total hardness, and numerous ion concentrations. Just as in the VoltiC Vario pro system, the analysers use the same liquid handling instruments, a common sample changer, and the same database. The system is controlled by the master software MagIC Net, while the titration software **tiamo** runs in the background. TitriC Vario pro has impressively short analysis times, uses little space, and gives high precision results.

TitriC Vario pro comes in three versions. All three systems determine temperature and conductivity, pH as well as p and m value, and analyze anions by ion chromatography.

In the basic system, TitriC Vario pro I, the content of Ca and Mg is measured by titrimetry. In TitriC Vario pro II and TitriC Vario pro III, cations are determined by ion chromatography. In addition, TitriC Vario pro III has a sample changer with the DisCover function for the automatic removal of the lid of the sample vessel. If required, additional determinations can be integrated into the «TitriC Vario pro» systems.

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The TitriC Vario pro III consists of an 856 Conductivity Module, two 800 Dosinos, an 802 Stirrer, a 905 Titrand, an 815 Robotic USB Sample Processor XL, and the 940 Professional IC Vario for anions and cations.

## Potentiostats and galvanostats

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### Energy from wastewater: the microbial fuel cell

Like all living beings, microorganisms meet their energy requirements by breaking down energy-rich substances. Humans make use of this in sewage treatment plants, where bacteria mineralize the organic pollutant load to a large extent. The microorganisms release electrons, which they transfer to electron acceptors such as oxygen, nitrate, and sulfate. If this transfer of electrons is from a mediator – i.e., an electron bridge – to a solid electron receptor such as an anode, an electric current will flow, provided there is also a cathode and a power consumer. This way, bacterial energy is directly converted to electrical energy. It is essential that the bacteria are in direct contact with the electrode in the form of a biofilm.

Initial results show that the degradation of pollutants in wastewater can be used to recover energy. The target is energy-neutral wastewater purification. For this, however, the electron transfer processes still need to be optimized, e.g., by increasing the size of the electrode surface. At present, work is being done with electrodes made up of countless conducting carbon fibers on which the bacteria sit. The electrochemical impedance spectroscopy capabilities of the Autolab PGSTAT128N with FRA32M module allow the electron transfer kinetics and interfacial properties to be monitored.

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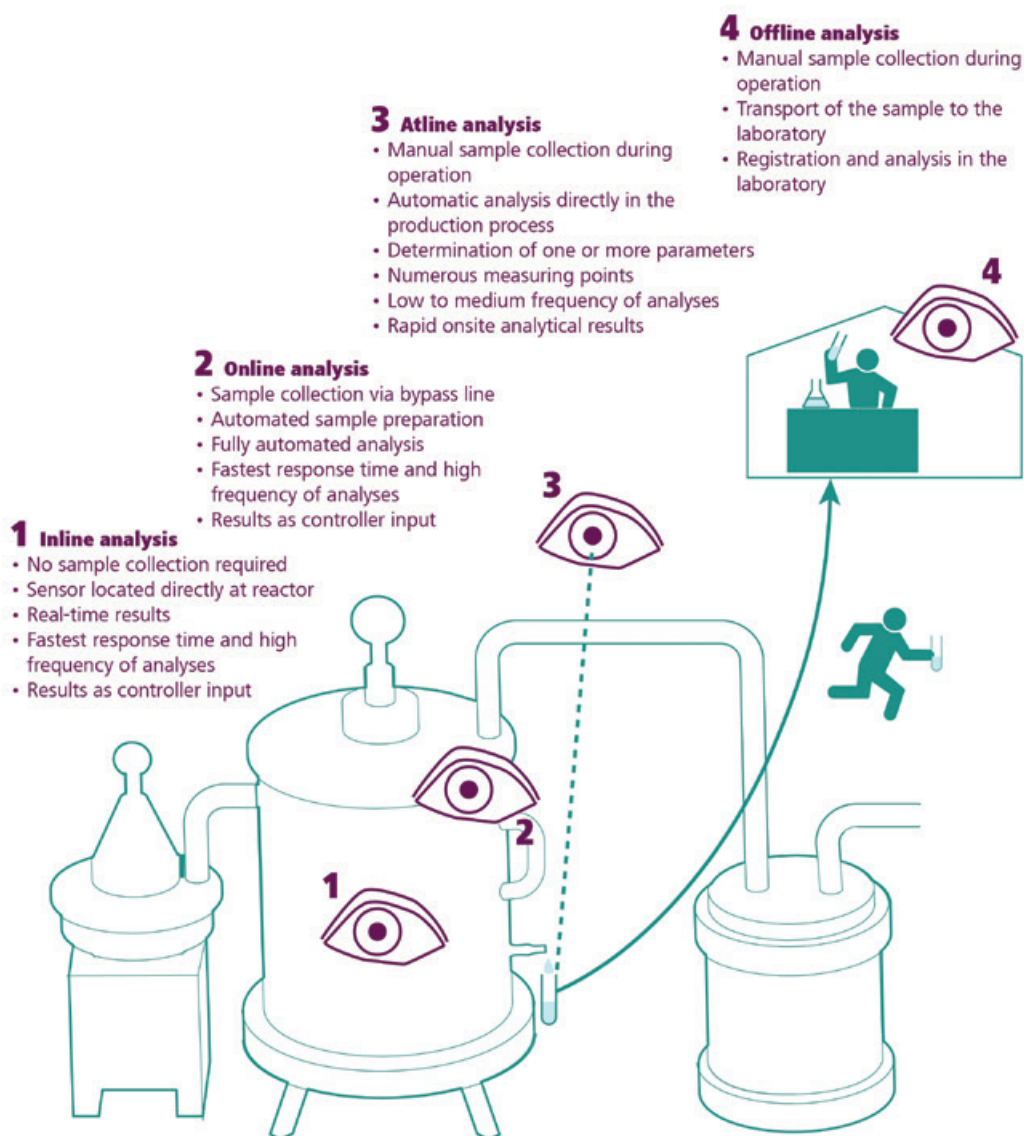
# Online and atline analysis systems from Metrohm Process Analytics

Online and atline Process Analyzers from Metrohm Process Analytics are the preferred solution for process monitoring in a wide range of industries. Using the complete range of modern ion analysis (pH value, conductivity, and redox potential titration, KF titration, photometry, ISE measurements, and voltammetry) Metrohm Process Analytics provides high precision results for any wet-chemical parameters you need right at your production line.

Metrohm Process Analytics has specialized in online and atline process analysis for over 40 years. With this vast

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

Metrohm Applikon, with Process Analyzers sold under the brand name Metrohm Process Analytics, is part of the Metrohm Group and represented in over 45 countries. Our regional and local presence offers knowledgeable support in sales, applications, project engineering, and start-up. We intend to be your process monitoring partner for years to come.





## Process analysis

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### Customized online and atline process control

Because of the outstanding dissolving properties of water a large number of organic and inorganic compounds accumulate in it. This requires powerful analysis that monitors the composition of the water continuously. With the Process Analyzers from Metrohm Process Analytics this is possible 24 hours a day, 7 days a week. The analyzers are used directly on-site, as close as possible to the process, and run without any operator intervention. Moreover, it makes no difference whether a single parameter is to be determined in a single sample stream or several different parameters are to be determined simultaneously in complex, multiple sample streams – whatever your requirement, Metrohm Applikon can offer you an appropriate online or atline Process Analyzer.

### Proven wet-chemistry methods

Most 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 Applikon 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

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 Analyzer

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<sup>+</sup> ISE, it is possible to measure sodium concentrations down to 1 µg/L. 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 Analyzer at concentrations as low as 1 µg/L.







#### **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 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.

#### **Chemical oxygen demand**

The chemical oxygen demand (COD) is one of the most important sum parameters for assessing wastewater pollution. Metrohm Process Analytics offers both titrimetric determination, described already on page 7, and also colorimetric determination: depending on the required detection limit, continuous COD determination can be performed by either the ADI 2045TI Process Analyzer or the Process Colorimeter ADI 2019.

#### **Heavy metals, phosphates, nitrates, and COD**

Numerous parameters need to be continuously monitored in industrial and municipal wastewaters. These include, for example, the heavy metals cadmium, lead, zinc, and cobalt as well as the anions nitrate, ammonium, phosphate, and sulfate. Metrohm Process Analytics has a wide range of analyzers available: while the ADI 2045VA Process Analyzer is designed specifically for determining heavy metals, the ADI 201Y and ADI 2045TI Process Analyzers perform the other analyses. In addition, Metrohm Process Analytics offers a large number of sample preparation systems that can be combined with any application, no matter how unusual that application might be.

#### **Iron in drinking water**

The taste of drinking water depends to a large extent on its origin and treatment. Water contains different amounts of magnesium, iron, sulfate, and carbonate, depending on whether it has passed through stone, clay or gravel sand. Iron concentrations above 2 mg/L have a significant effect on taste. Many water suppliers use sand filters to remove the iron. Alert Ion Analyzers, developed specifically for water analysis, ensure continuous monitoring of the filter performance. Iron can be detected colorimetrically in the presence of a color indicator – and this can be done every six minutes.

## II. Soil

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### Determination of pH value and conductivity

The pedosphere is the name given to a highly complex boundary area where the lithosphere, hydrosphere, atmosphere and biosphere coexist. As a multiphase system, the pedosphere consists predominantly of soil mineral matter, approximately equal proportions of soil air and soil water, and a small amount of organic matter. The pedosphere forms the key basis of life for plants, animals, and humans. Harmful substances contained in it come mainly from weathering, cultivation, or the air.

#### Soil pH value – soil reaction according to ISO 10390

The pH value of a soil sample is the most frequently determined parameter in soil analysis. It is the characteristic value of what is known as «soil reaction» and allows soils to be classified according to their acidity and alkalinity.

Determination of the pH value provides information about the acid or base action of the soil solution. This in turn is enormously important for the nutrient supply and microbial activity of the soil. For example, many metals (trace elements) are considerably more mobile in acidic soils. If the soil pH values are very low, toxic levels can soon be reached and these can damage the roots of plants. On the other hand, excessively high pH values quickly lead to a shortage of trace elements because of immobilization.

The flat membrane electrode is ideal for pH measurements in sediment-containing sample solutions.

A simple method for determining the pH value is described in ISO 10390. It describes the slurring of an air-dried and sieved (max. 2 mm sieve) soil sample with distilled water and subsequent measurement. Alternatively, extraction can be performed using 0.01 molar  $\text{CaCl}_2$  or 1 molar KCl. The cations in these solutions displace the protons that are absorbed on the ion exchangers of the soil as quantitatively as possible.



914 pH/Conductometer: ideal for routine use in the lab and as robust companion in the field





#### **Determination of electrical conductivity in soil samples according to ISO 11265**

The determination of conductivity provides qualitative information about the amount of dissolved salts in the soil. It allows conclusions about the ability of the soil water to mobilize mineral substances in the soil.

To determine electrical conductivity, a weighed-out quantity of a dried soil sample is shaken up with a defined volume of distilled water and then measured directly.

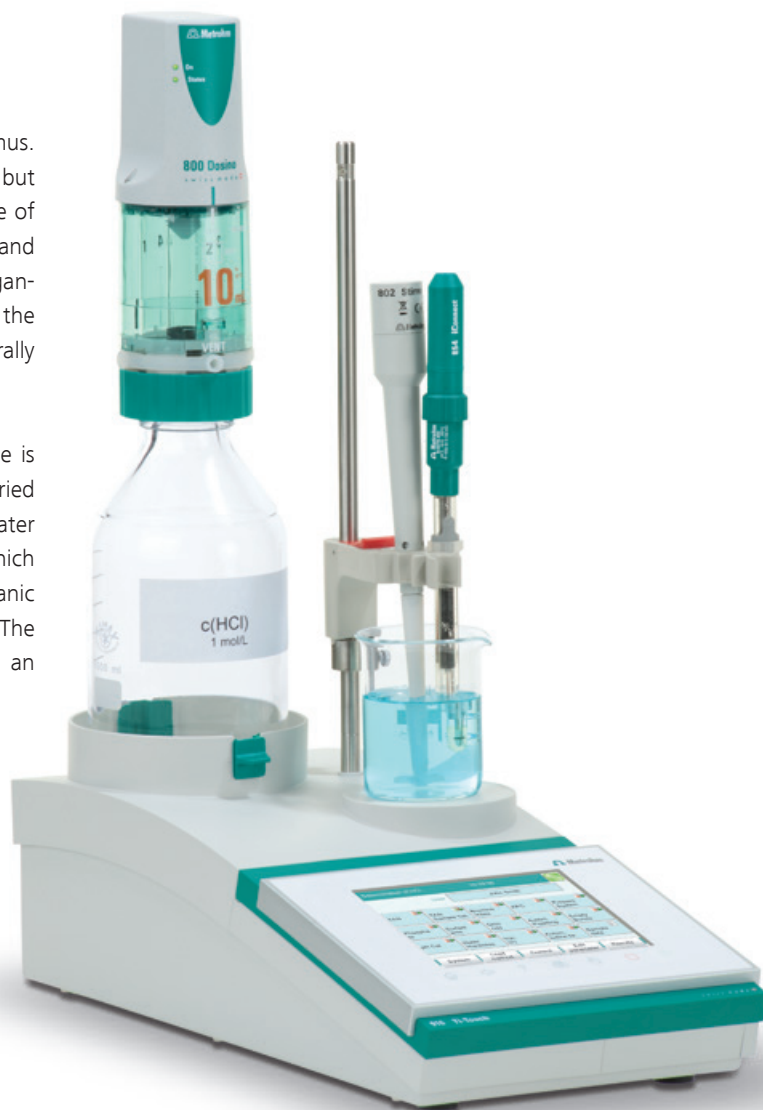


## Titration

### Total organic carbon (TOC value)

Dead soil organic matter is known collectively as humus. Humus does not form a homogeneous soil fraction, but exists in a variety of forms, depending on the degree of decomposition. It provides plants with nutrients and forms an important habitat for many soil-dwelling organisms. The most important component of humus is the total organic carbon (TOC), which is also used generally as a measure of the humus content.

The determination of the TOC value of a soil sample is based on the Walkley-Black method. For this, an air-dried soil sample is treated (after determination of the water content) with a potassium dichromate solution to which sulfuric acid has been added. As a result, all the organic carbon constituents in the soil sample are oxidized. The unconsumed dichromate is then back-titrated with an iron sulfate solution.



Stand-alone Titrator 916 Ti-Touch for routine analysis







#### Important soil parameters – overview

Method	Sample preparation	Detection type	Titrant
<b>pH value</b> (ISO 10390)	Slurrying	Direct measurement	–
<b>pH value</b> for the determination of the leaching behavior of inorganic components from waste (DIN CEN/TS 14997)	Continuous pH control to determine the influence of pH value on leaching behavior	Direct measurement (with continuous eluate analysis)	–
<b>Conductivity</b> (ISO 11265)	Slurrying	Direct measurement	–
<b>Total organic carbon (TOC), Walkley-Black method</b>	$K_2Cr_2O_7/H_2SO_4$ digestion	Visually with barium diphenylamine sulfonate	1 mol/L $FeSO_4$ (acidic)
<b>Aluminium</b>	Extraction	Visually, phenolphthalein	0.02 mol/L NaOH
<b>Carbonate content, Piper method</b> (also known as rapid titration or acid neutralization method)	Soil sample is shaken with 0.2 mol/L HCl and allowed to settle; 10 mL of the supernatant solution is back-titrated with NaOH	a) Photometrically with phenolphthalein b) Potentiometrically, SET titration to pH 7.8	0.1 mol/L NaOH
<b>Acidity</b> «Exchangeable acidity» (H + Al)	Ion exchange with 1 mol/L KCl	a) Photometrically with phenolphthalein b) Potentiometrically, SET titration to pH 7.6	0.025 mol/L NaOH
<b>Total cyanide and easily released cyanide</b> (ISO 11262)	Distillation	a) Photometrically with phenolphthalein b) Potentiometrically	0.005 mol/L $AgNO_3$
<b>Soluble anions carbonate/bicarbonate (alkalinity)</b>	Extraction with $CO_2$ -free distilled Water	SET titration to pH 8.4 and 4.4	0.1 mol/L HCl

## Ion chromatography

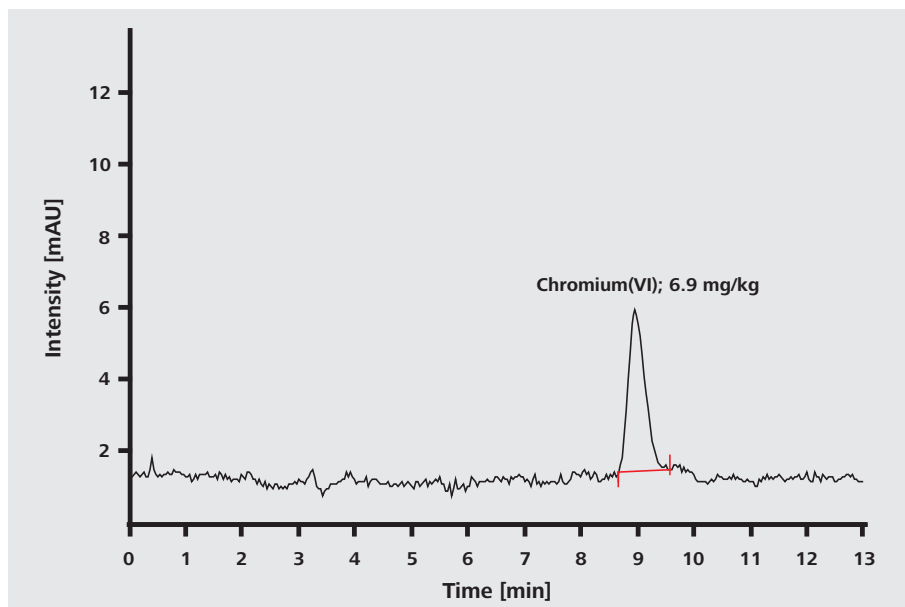
### Chromate in soil samples

Chromium occurs primarily in the stable oxidation states Cr(III) and Cr(VI). The oxidation state determines the biological and toxicological properties, which could hardly be any more different: Cr(III) is one of the essential trace elements and plays an important role especially in the metabolism of fats and glucose, whereas hexavalent chromium is very toxic and carcinogenic.

Chromium is present in different concentrations in all types of soil and rock. It usually occurs in the cationic and less bioavailable trivalent form; it can, however, also occur as toxic and very mobile chromium(VI) anion – usually as a result of anthropogenic input. Because of the differences in toxicity, the total concentration of chromium is of less interest than the concentration of chromate.

Ion chromatography can detect chromate in the soil down to  $\mu\text{g/L}$  levels. Here, the relatively large, doubly charged chromate anion is separated from the other anions on an anion-exchange column and then converted by post-column reaction with 1,5-diphenylcarbazide solution to form a reddish-violet complex that is analyzed at 540 nm with a UV/VIS detector.

The sample preparation of soil samples is a demanding task. It is essential to ensure that the extraction solution releases the chromate from the samples without there being any change in the oxidation state of the chromate. For most soil samples, alkaline digestion according to EPA 3060A or ISO EN 15192 is recommended. Before ion chromatographic determination, filtering with  $0.45\ \mu\text{m}$  filters is required. This can also be automated conveniently with the use of an Inline Ultrafiltration cell.



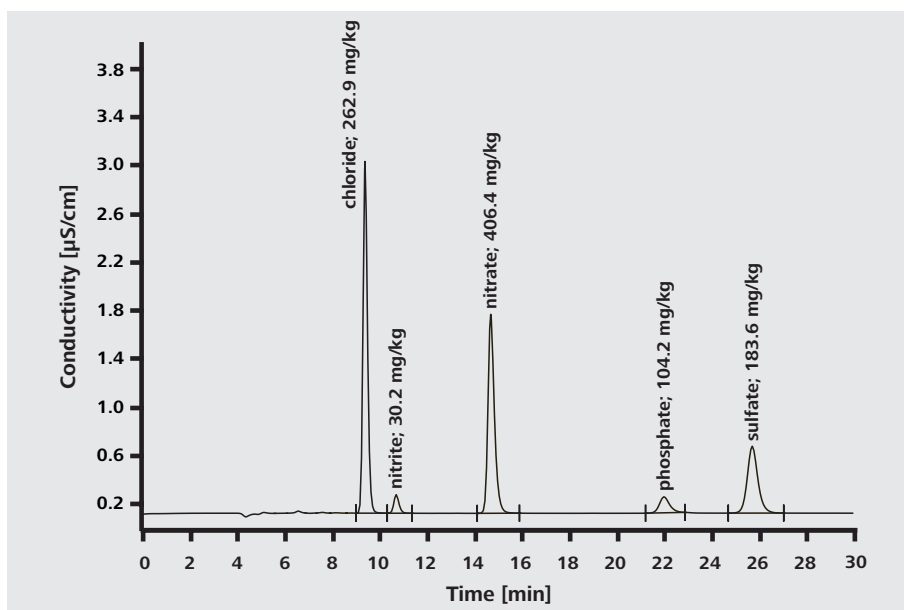
Worked-up soil sample (2.5 g soil in 100 mL 0.25 mol/L NaOH/0.14 mol/L  $\text{Na}_2\text{CO}_3$ , then dilute with ultrapure water 1:10); column: Metrosep A Supp 5 - 250/4.0; eluent: 15 mmol/L  $\text{Na}_2\text{CO}_3$ , 10 mmol/L NaOH, 0.7 mL/min; sample volume: 100  $\mu\text{L}$ ; post-column derivatization with 0.5 g/L 1,5-diphenylcarbazide, 10% methanol, 0.5 mol/L  $\text{H}_2\text{SO}_4$ ; flow rate post-column reagent: 0.5 mL/min; UV/VIS detection at 540 nm



### Anions and cations in soil samples

The nutrient content in soil samples determines plant growth and is of great importance especially with regard to agricultural use. Of prime interest here are the concentrations of the main nutrient elements (macronutrient elements) nitrogen, phosphorus, potassium, calcium, magnesium, and sulfur.

Ion chromatography with conductivity detection enables rapid determination of the nitrogen components nitrate, nitrite, and ammonium, and also of the ions sulfate, phosphate, calcium, magnesium, and potassium. Sample preparation includes aqueous extraction of the soil samples.



Anion determination in a worked-up soil sample, 10 g seed compost in 100 g water, then extracted for 10 minutes in an ultrasonic bath, diluted with ultrapure water 1:10 (v/v), and finally filtered with 0.45 µm filters and RP cartridges; column: Metrosep A Supp 5 - 250/4.0 eluent: 3.2 mmol/L  $\text{Na}_2\text{CO}_3$ , 1.0 mmol/L  $\text{NaHCO}_3$ , 5% acetone, 0.7 mL/min; column temperature: 30 °C; sample volume: 20 µL; conductivity detection after sequential suppression



940 Professional IC Vario with 944 Professional UV/VIS Detector Vario and 943 Professional Reactor Vario: the ideal system for chromat analysis



# Voltammetry

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## Trace elements and harmful pollutants in the soil

The determination of the nutrient content in the soil requires not only ion chromatographic analysis of the main nutrient elements, but also determination of the essential trace elements: iron, manganese, zinc, and copper. This can be achieved very accurately and sensitively by voltammetry. Moreover, voltammetry is suitable for analyzing harmful heavy metals such as lead, cadmium, chromium, mercury, uranium, and zinc in the soil.

In contrast to water analyses, ion analysis in soils is usually preceded by extraction or digestion to transfer the ions into the aqueous solution. Various sample prepara-

tion methods are described in standards (e.g., ISO 12914). The extracts obtained can usually be determined directly by voltammetry.

Another application of voltammetry is the determination of organophosphorus pesticide residues, such as, for example, diazinon, malathion, parathion-methyl, and parathion, according to AOAC 970.53. Through extraction with organic solvents the electrochemically active substances are separated from the soil matrix and then enriched by adsorption on the HMDE and determined by reduction.





## Potentiostats and galvanostats

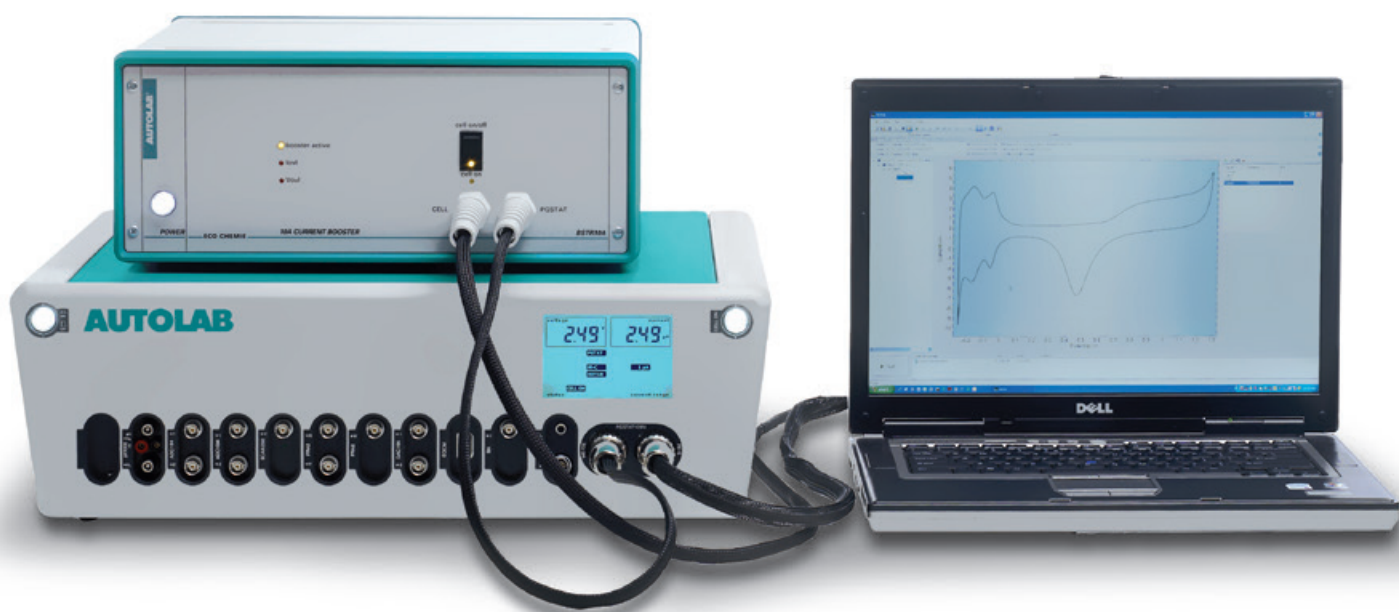
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### Analysis for the electroremediation of contaminated soils

Soils contaminated with heavy metals and organic compounds represent a serious risk to the environment, which is why cost-effective and environmentally compatible remediation of contaminated sites is becoming increasingly urgent. In situ methods where contaminated soils are treated without being excavated are the state of the art. A very promising method is electroremediation (also known as electrochemical remediation), where a series of anodes and cathodes installed in the soil body and connected to a direct-current source induce an electrical field, under the influence of which electrokinetic transport and redox processes take place. As a result, heavy metals are reduced on the cathode and harmful organic

substances, such as phenols, aromatic amines, or halogenated hydrocarbons, are oxidized on the anode. Electroremediation is ideal for fine-grained clay, loam, or silt soils with a high water-retention capacity, where other in situ remediation techniques usually fail.

The first Autolab potentiostats/galvanostats were developed exactly two decades ago for this type of application. By combining a PGSTAT128N potentiostat/galvanostat (cyclic voltammetry and galvanostatic analysis) and a booster it is possible to track the redox reactions – the oxidation of organic compounds and the reduction of heavy metals – taking place in the soil body.



Autolab PGSTAT128N with BSTR10A 10A Current Booster

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### III. Air

On average about 300,000 m<sup>3</sup> air pass through a person's respiratory system in the course of a lifetime. In this way, impurities in the atmosphere directly enter the lungs. Especially dangerous are the aerosols that contain particles with diameters of less than 10 µm – also known as particulate matter. These are airborne heterogeneous mixtures of substances made up of minute particles, some of which are solid and some liquid. The smaller these particles are, the deeper they go into the lungs. Once they reach the place where the gas exchange occurs, the pulmonary alveoli, there is just one micron of tissue between them and the blood stream.

Aerosols come both from natural sources (volcanic eruptions, sea spray, desert dust, fire, biogenic input) and from anthropogenic sources (burning of fossil fuels, industrial

production). By reflecting sunlight and acting as condensation seeds for cloud formation, they influence our climate and weather.

The chemical composition of aerosols is highly complex and not yet fully understood. To estimate the effects of aerosols on health and climate, it is essential to know their chemical composition. Sampling is done using two different types of aerosol collector. The first type are filter collectors that are based on the deposition of suspended particles on surfaces; they usually require a pump, are operated in offline mode, and supply data over prolonged accumulated periods. The second type are powerful aerosol collectors such as PILS or MARGA that work primarily in online mode and provide semicontinuous data.

## Filter methods

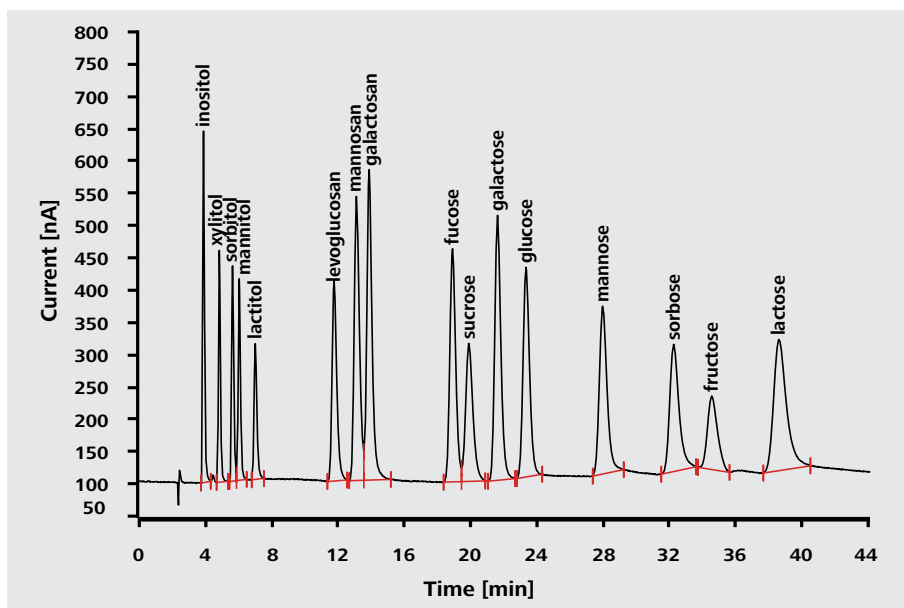
The particulate matter contained in the air is collected on filters with a certain air flow over a defined period of time. Sampling is usually in accordance with DIN EN 12341. The composite air samples of particulate matter are extracted and the extract is then analyzed using ion chromatography (IC) or voltammetry (VA).

### Saccharidic tracers in particulate matter by IC

The anhydrosugars levoglucosan, mannosan, and galactosan are produced when cellulose and hemicellulose are burnt and act as tracers for the combustion of biomass. By contrast, the sugar alcohols arabitol and mannitol are tracer substances for biological processes: when fungi fling spores into the air, the concentration of mannitol in the aerosol increases. Studies in the Amazon rain forest showed that the biogenic fraction consisted of fungal spores and formed up to 50% of the ambient aerosol.

Thus, concentration profiles of these saccharidic tracers make it possible to obtain indications of sources of aerosols. For example, analysis of the saccharide composition in summer filters shows a significantly higher proportion of sugar alcohols. In winter filters, by contrast, there is a predominance of anhydrosugars, especially levoglucosan.

Following direct water extraction by the aerosol filters, the saccharidic tracers are separated by ion chromatography and determined reliably down to lower  $\text{ng/m}^3$  levels by way of pulsed amperometric detection (PAD). The IC-PAD method requires no derivatization, can be automated easily and is suitable for routine use with large sample series.



Determination of saccharidic tracers; columns: Metrosep Carb 2 - 150/4.0; eluent: 5 mmol/L sodium hydroxide, 2 mmol/L sodium acetate 0.6 mL/min; column temperature: 40 °C; sample volume: 20  $\mu\text{L}$ ; PAD measuring mode (gold working electrode)

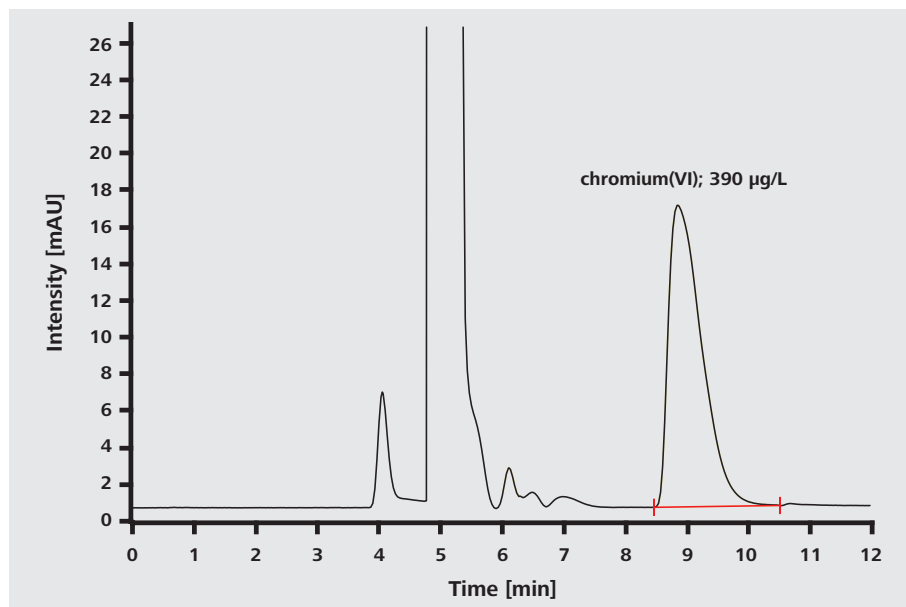


### Chromium(VI) in the particulate matter of indoor air – IC method according to ASTM D6832

When breathed in, water-soluble chromium(VI) particles in the PM<sub>2.5</sub> fraction pass all the way through to the pulmonary alveoli. There, they penetrate the extremely thin tissue and enter the liver and kidney cells by way of the blood plasma. Starting out from the red cells, Cr(VI) thus interacts with the cellular protein molecules of the DNA.

Like other carcinogenic compounds, chromium(VI) is subject not to an occupational exposure limit, but to the ALARA principle of minimization (as low as reasonably achievable). It requires the emissions of carcinogenic substances to be reduced to the minimum. This calls not only for speciation analysis, but also for detection limits in the low µg/L range.

The method described in ASTM D6832 for chromium(VI) determination in the particulate matter of indoor spaces describes an ion chromatographic separation of the chromium(VI) species with post-column derivatization and spectrophotometric detection. The sampling and sample preparation techniques chosen are such that no transformation occurs between trivalent and hexavalent chromium compounds. Furthermore, a distinction can be made between soluble and insoluble chromium(VI) compounds by choosing the appropriate extracting agent.



Determination of the insoluble chromium(VI) content in filter extracts of an air sample; ultrasound-assisted extraction with 3% Na<sub>2</sub>CO<sub>3</sub> and 2% NaOH with a subsequent 1:1 (v/v) dilution of the extract; column: Metrosep A Supp 10 - 250/4.0; eluent: 0.25 mol/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.05 mol/L NH<sub>4</sub>OH, 0.6 mL/min; column temperature: 25 °C; sample volume: 1000 µL; post-column derivatization with 2 mmol/L 1,5-diphenylcarbazide, 10% methanol, 0.5 mol/L H<sub>2</sub>SO<sub>4</sub>; flow rate post-column reagent: 0.2 mL/min; UV/VIS detection at 540 nm



**Heavy metals in the particulate matter by voltammetry**

The heavy metals (e.g., lead, cadmium, and zinc) contained in particulate matter and dust deposits not only act directly on the respiratory system through inhaled air, but can also accumulate in soil and water as a result of wet and dry deposition from the air and thus enter the food cycle, and from there make their way into the organism. Apart from having a carcinogenic effect, heavy metals especially damage the kidneys, liver, nervous system, and cardiovascular system.

Although the ambient air concentrations of heavy metals have decreased considerably since the ban on leaded gasoline, particulate matter samples from sites exposed to traffic and industry still show noticeable amounts of lead, arsenic, and cadmium. Directive 2008/50/EC of the European Parliament and of the Council on ambient air quality and cleaner air sets limits and targets for various concentrations of harmful substances in the air.

With the help of voltammetry, heavy metals in the air can be determined right down to trace levels.

## Semicontinuous methods

### PILS – Particle Into Liquid Sampler

Compared with the filter methods, the Particle Into Liquid Sampler (PILS) allows a much higher time resolution. Semicontinuous measurements are possible approximately every 15 minutes. This high time resolution allows changes in the aerosol composition to be correlated with meteorological and other data. Furthermore, there is no need for complicated and error-prone manual sample preparation, and no hassle of storing samples.

The way PILS works is simple. At the intake, a size-selective glass spiral (cyclone) limits the particle size of the aerosols to a maximum of 1, 2.5 or 10  $\mu\text{m}$  ( $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$ ,  $\text{PM}_{10}$ ), as required. The aerosols then enter a condensation chamber, where they meet a supersaturated water vapor phase. Within a very short time they grow into droplets, are separated out, and transported to the ion chromatograph or the voltammetric measuring cell by a carrier fluid.

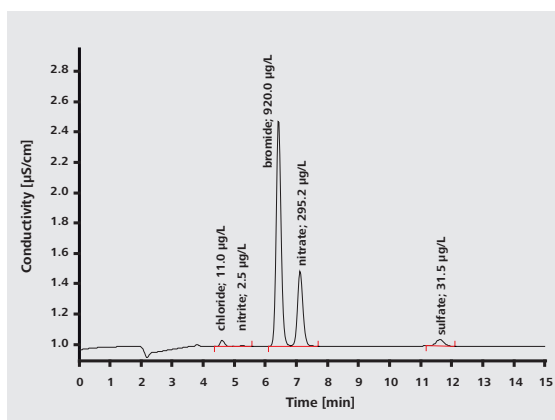
PILS can be connected directly to a wide range of analyzers. Apart from coupling to ion chromatographs and voltammetric measuring stands, which is described in this brochure, coupling to TOC or ICP analyzers is also widespread. Whereas the former determines the total organic carbon in the aerosol, ICP is used for multi-element analysis. Offline sampling with an autosampler is also possible.

### Semicontinuous determination of anions and cations by PILS-IC

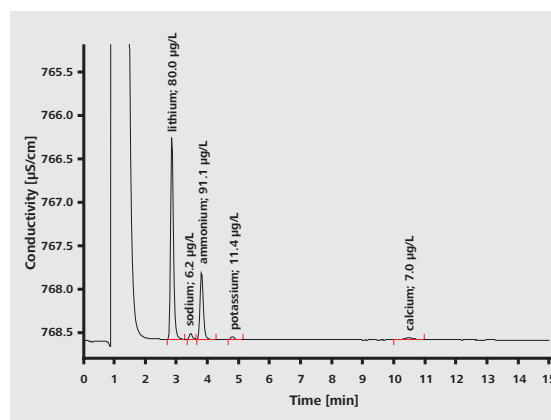
Coupling with ion chromatography allows climate-related water-soluble anions and cations in the aerosol to be determined. This enables important conclusions to be drawn about the precursors and thus about the question of whether particles are emitted directly – as in the case of the primary sea salt aerosols ( $\text{NaCl}$ ) – or whether the materials are secondary aerosols that are not formed until a chemical reaction has taken place (e.g., sulfate aerosols).



The Particle Into Liquid Sampler. PILS coupled with IC and VA can be used to measure the ionic substances of the aerosols.



Anions in an aerosol sample ( $\text{PM}_{2.5}$ ) from outside air; the internal standard is  $\text{LiBr}$ ; column: Metrosep A Supp 5 - 100/4.0; eluent: 3.2 mmol/L  $\text{Na}_2\text{CO}_3$ , 1.0 mmol/L  $\text{NaHCO}_3$ , 0.7 mL/min; sample volume: 250  $\mu\text{L}$ ; conductivity detection after sequential suppression

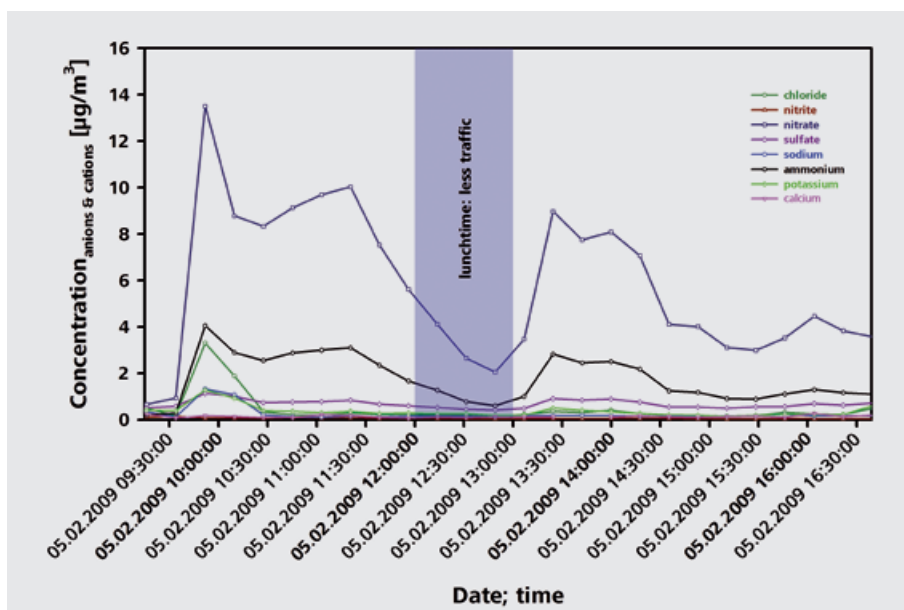


Cations in an aerosol sample ( $\text{PM}_{2.5}$ ) from outside air; the internal standard is  $\text{LiBr}$ ; column: Metrosep C 4 - 100/4.0; eluent: 1.7 mmol/L  $\text{HNO}_3$ , 0.7 mmol/L dipicolinic acid, 0.9 mL/min; sample volume: 250  $\mu\text{L}$ ; Conductivity detection without sequential suppression

### Anions and cations by PILS-IC

Semicontinuous determination of anions and cations in atmospheric aerosols allows high time resolution, which enables the concentration to be recorded over a prolonged period. Sudden changes in aerosol composition can

be detected immediately. The falling nitrate and ammonium concentrations between 12:00 and 1.00 p.m. are a consequence of the lower volume of traffic during the lunch break.

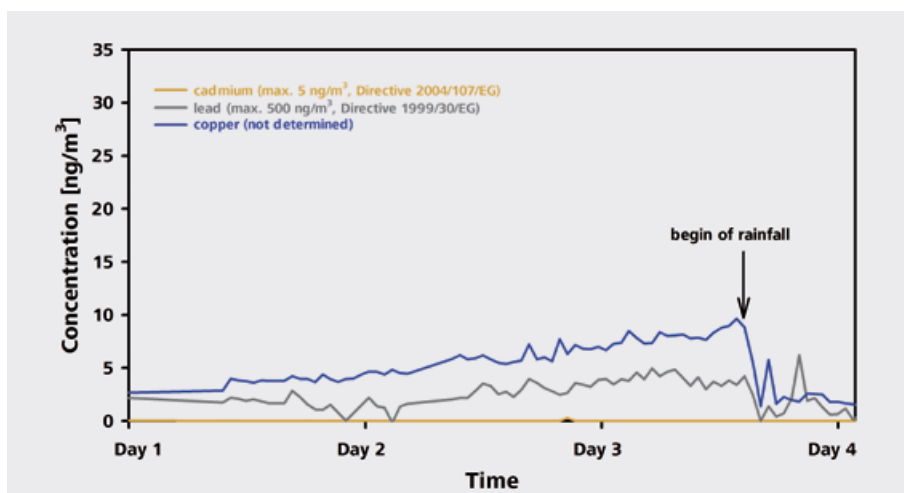


Semicontinuous ion chromatographic determination of anion and cation concentrations in air samples from Herisau (Switzerland) by a PILS sampling system

### Heavy metals by means of PILS-VA

The combination of the PILS aerosol collector with the 797 VA Computrace allows semicontinuous determination of various heavy metals (Cd, Pb, Zn, Cu, Ni, Co, etc.) in particulate matter. The high time resolution picks up even the smallest changes in the chemical composition

of the aerosols: the concentrations of copper and cadmium in the air increase steadily over several days until it starts to rain and a large proportion of the copper and cadmium are washed out of the air (wet deposition).



Semicontinuous voltammetric determination of heavy metal concentrations (Cd, Pb, and Cu) in air samples from Herisau (Switzerland) by a PILS sampling system

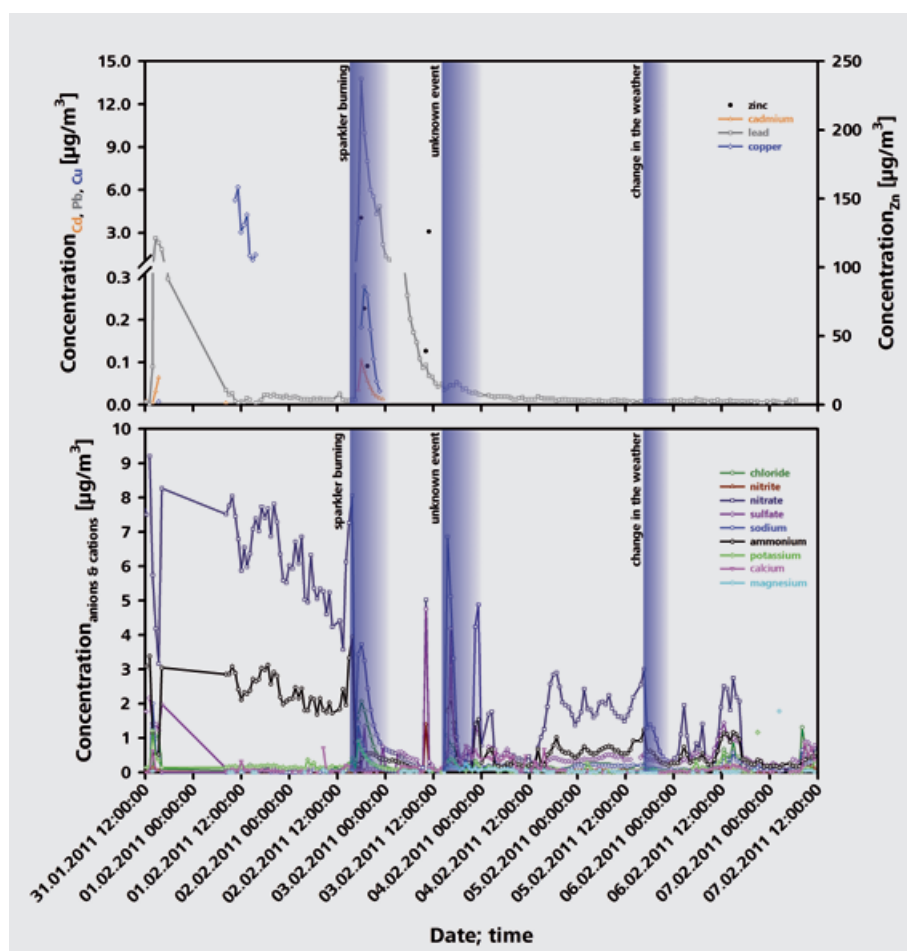




### Standard ions and heavy metals by PILS-IC-VA

Simultaneous coupling with several analyzers is also possible: in PILS-IC-VA the particles brought into solution are conveyed in three streams to a two-channel ion chroma-

tograph for anion and cation determination and to a voltammetric measuring stand for determination of the heavy metal ions.



Semicontinuous ion chromatographic determination of the anion and cation concentrations and voltammetric determination of the heavy metal concentrations in air samples from Herisau (Switzerland). To simulate contamination events, sparklers that had been previously immersed in heavy metal salt solutions were burnt.

### MARGA – Monitor for AeRosols and Gases

While the PILS aerosol collector enables semicontinuous determination of water-soluble ions in aerosol particles, MARGA (Monitor for AeRosols & Gases in Ambient air) offers the option of also analyzing the composition of the water-soluble gas phase. As in the PILS system, air is sucked into the analyzer through a size-selective particle separator. Together, gases and aerosols enter a rotating gas-phase diffusion separator (denuder), where the former are absorbed in a thin layer of water ( $\text{NH}_4^+$ ,  $\text{SO}_x$ ,  $\text{NO}_x$ ,  $\text{HCl}$ ), and sent to the ion chromatograph for determination of the anions and cations. From the denuder, the aerosols go to the Steam-Jet Aerosol Collector (SJAC),

where they meet a supersaturated steam phase, absorb an increasing amount of water as condensation seeds, grow as a result of this, and are finally separated out mechanically in a glass spiral (cyclone). The resulting solution is collected, and its anion and cation content is determined hourly by the integral ion chromatograph.

A MARGA system provides exact results every hour. Because the system can work for days on end without the addition of new solutions, MARGA is ideal for field use in remote regions.



The MARGA system at a glance. At the top is the box with the air inlet, diffusion separator, Steam-Jet Aerosol Collector (SJAC), eluent container and some pumps; in the middle are the sample delivery and the two ion chromatographs for determination of anions and cations, along with an integrated computer. The bottom shelf accommodates various storage containers, an uninterruptible power supply, and a vacuum pump.

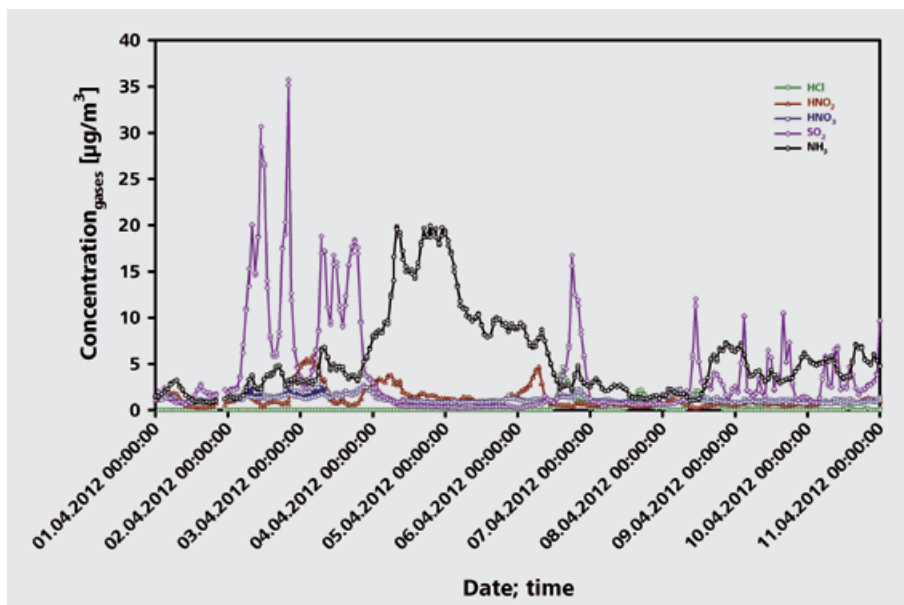


**Disclaimer:** The EPA Environmental Technology Verification Program (ETV) Name and/or Logo does not imply approval or certification of this product, nor does it make any explicit or implied warranties or guarantees as to product performance. Information on the performance characteristics of Metrohm Process Analytics ADI 2080 MARGA can be found at [www.epa.gov/etv](http://www.epa.gov/etv), or call Metrohm Applikon at +31 10 29 83 555 to obtain a copy of the ETV verification report.

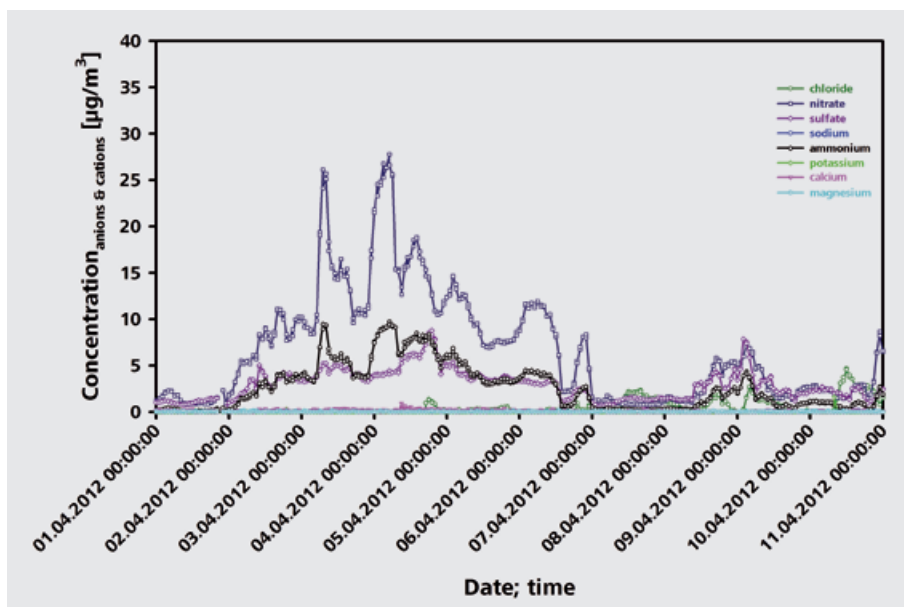
### MARGA – simultaneous monitoring of gases and aerosols

MARGA is a combination of sample preparation system and online ion chromatographs, it is able to determine,

simultaneously, the gas and aerosol composition of the ambient air fully automatically every hour.



Changes over time in the concentration of some gases in the ambient air in Schiedam (Netherlands), April 2012. The concentration curve of the gases was determined by semicontinuous IC analyses of the aqueous phases from the rotating gas diffusion separator.



Changes over time in the ionic aerosol constituents in the ambient air in Schiedam (Netherlands), April 2012. The aqueous samples for ion analysis come from the Steam-Jet Aerosol Collector (SJAC).

## Potentiostats and galvanostats

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### From greenhouse gas to a source of carbon – electrochemical reduction of CO<sub>2</sub>

Atmospheric carbon dioxide is a climate-related gas that is produced as a product of oxidation when organic material is burnt. Reducing the concentration of CO<sub>2</sub> in the atmosphere is a worldwide target. One promising approach is using the CO<sub>2</sub> in the atmosphere as a raw material source, e.g., to synthesize raw materials for fuels or chemicals.

The principle is a formal reversal of combustion according to the photosynthesis model. In the process, CO<sub>2</sub> is reduced by electrical direct current in the presence of various catalysts to produce reactive carbon monoxide or methanol. By varying the catalysts on the electrodes it is possible to synthesize a large number of organic products, such as formic acid, formaldehyde, and higher alcohols, as energy sources.

The PGSTAT 302N potentiostat/galvanostat makes it possible to track the reactions taking place on the catalyst surfaces and thereby provides an indispensable tool for optimizing the catalysts.

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## Metrohm Quality Service – Service you can rely on

### Reliable results for the lifetime of your analytical instruments

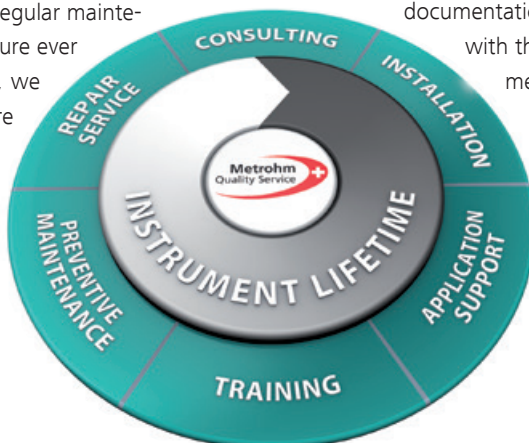
Environmental analysis is a key component of analytical chemistry and covers the analysis of water, soil, and air samples. Whoever is responsible in the laboratory for the accuracy of the results must not make compromises. Fortunately, systems installed and maintained by professionals on a regular basis all but eliminate the threats of instrument failure and lost profits.

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

### Metrohm Compliance Service

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

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



### Metrohm Quality Service

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

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

Metrohm Quality Service	Customer benefits
Metrohm Care Contracts	<ul style="list-style-type: none"> <li>Minimizes downtime through preventive maintenance</li> <li>Cost control and savings through free or discounted replacement materials and consumables</li> <li>Guaranteed reaction times and rapid on-site repair</li> <li>Documented instrument certification as an ideal preparation for audits</li> </ul>
Metrohm Software Care	<ul style="list-style-type: none"> <li>High data security and maximum system performance through regular, professional software maintenance</li> </ul>
Metrohm Compliance Service	<ul style="list-style-type: none"> <li>Customized services and documentation for analytical instrument qualification (AIQ)</li> <li>Professional start-up (IQ/OQ or Certified Installation) and requalification or recertification by specifically trained employees</li> </ul>
Metrohm Remote Support	<ul style="list-style-type: none"> <li>Quick resolution of software and application issues directly at the workplace</li> </ul>
Metrohm Dosing Test	<ul style="list-style-type: none"> <li>Calibration of burettes (e.g., dosing and exchange units) with certification</li> <li>Accurate measurement results</li> <li>Verification documentation for compliance with regulations and efficient audits</li> </ul>
Metrohm Repair Service	<ul style="list-style-type: none"> <li>Rapid availability of repaired instruments thanks to decentralized repair workshops around the world and a central workshop at the manufacturer site</li> <li>Highly qualified service technicians ensure sustainable repair success</li> <li>Rapid resolution of problems and minimized downtimes through on-site emergency services and express repairs</li> </ul>
Metrohm Spare Parts	<ul style="list-style-type: none"> <li>Original spare parts, made in Switzerland and available worldwide</li> <li>Short delivery times through warehousing from local distributors</li> <li>Investment security through ten-year spare parts guarantee after discontinuation</li> </ul>
Metrohm Application Support	<ul style="list-style-type: none"> <li>Free access to the Metrohm Application Finder (<a href="http://www.metrohm.com/en/applications/">www.metrohm.com/en/applications/</a>) with more than 1800 applications (Application Bulletins, Application Notes, monographs, technical posters, and technical articles)</li> <li>Rapid and professional resolution of any application issues through personal consultations with our specialists by e-mail, telephone, or remote support</li> <li>Support for the solution of complex analytical problems, as well as method optimization on-site or at our application laboratories</li> </ul>
Metrohm Training Programs	<ul style="list-style-type: none"> <li>Basic and advanced training with local representatives, at the Metrohm Academy or directly on-site</li> <li>Efficient and proper use of all analytical methods, as well as results reliability through competently trained users</li> <li>Training documentation and certificates for trouble-free audits</li> </ul>



## Ordering information

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### pH/Ion measuring

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 for pH and ion measuring with Touch Control including iUnitrode
6.0502.150	Ion-selective electrode F <sup>-</sup>
6.0502.180	Ion-selective electrode Ag/S
6.0750.100	ISE Reference electrode
6.2104.020	Plug-in head G – plug F, 1 m
6.2106.020	Plug-in head B – plug B, 1 m

### Conductivity measurement

2.856.0110	856 Conductivity Module with Touch Control and five-ring conductivity measuring cell $c = 0.7 \text{ cm}^{-1}$
2.912.0210	912 Conductometer Lab, 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 Pt 1000 for 856 Conductivity Module
6.0915.130	Five-ring conductivity measuring cell, $c = 1.0 \text{ cm}^{-1}$ with 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

#### (Alkalinity, COD, chloride, Ca/Mg hardness, TOC)

2.905.0010	905 Titrando
2.800.0010	800 Dosino
2.801.0040	801 Stirrer
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	Aquatrode plus with Pt 1000
6.0277.300	iAquatrode plus with Pt 1000, plug-in head U, without cable
6.0470.300	iAg-Titrode
6.0471.300	iPt-Titrode
6.0510.100	Combined ion-selective electrode Ca <sup>2+</sup>
6.0750.100	ISE Reference electrode
6.2104.020	Plug-in head G – plug F, 1 m
6.2106.020	Plug-in head B – plug B, 1 m
6.2104.600	Plug-in head U – plug F + 2 × B (2 mm), 1 m

#### SET Titration soil analysis (Carbonate/bicarbonate/exchangeable Acidity)

2.877.0010	877 Titrino plus
2.801.0010	801 Stirrer
2.141.0100	USB Thermal printer Neo's
6.0221.600	Ecotrode Gel with temperature sensor, plug-in head U
6.2104.600	Plug-in head U – plug F + 2 × B (2 mm), 1 m
6.3026.220	Exchange unit 20 mL





## **Ion chromatography**

### **Oxyhalides and standard ions in mineral water**

2.940.2500	940 Professional IC Vario TWO/SeS/PP
2.850.9010	IC Conductivity Detector (2 x)
2.858.0020	858 Professional Sample Processor – Pump
2.941.0010	941 Eluent Production Module
6.2041.440	Sample Rack 148 x 11 mL
6.1006.630	Metrosep A Supp 7 - 250/4.0
6.1011.030	Metrosep RP 2 Guard/3.5
6.2842.000	MSM-HC Rotor A
6.6059.312	MagIC Net 3.1 Professional
6.05330.010	IC Equipment: Inline Ultrafiltration 2 – pull mode
6.05330.110	IC Equipment: Inline Ultrafiltration 2 – push mode

### **Bromate in drinking water**

2.930.2160	930 Compact IC Flex Oven/Deg
2.943.0110	943 Professional Reactor Vario
2.944.0010	944 Professional UV/VIS Detector Vario
2.858.0020	858 Professional Sample Processor – Pump
2.800.0010	800 Dosino
6.3032.150	Dosing Unit 5 mL
6.2041.440	Sample Rack 148 x 11 mL
6.1031.410	Metrosep A Supp 16 - 100/4.0
6.1031.500	Metrosep A Supp 16 Guard/4.0
6.6059.311	MagIC Net 3.1 Compact

### **Aliphatic amines in wastewater**

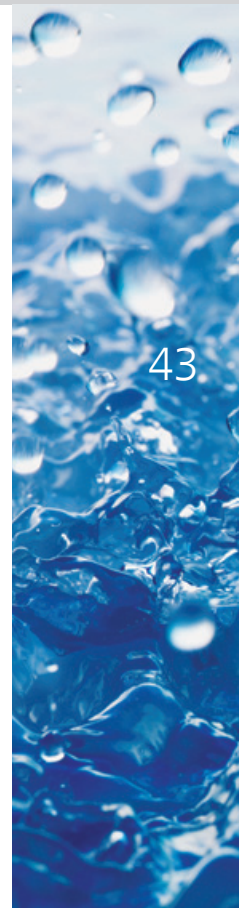
2.930.1160	930 Compact IC Flex Deg
2.850.9010	IC Conductivity Detector
2.919.0020	919 IC Autosampler plus
6.1050.410	Metrosep C 4 - 100/4.0
6.1050.500	Metrosep C 4 Guard/4.0
6.6059.311	MagIC Net 3.1 Compact
6.05330.010	IC Equipment: Inline Ultrafiltration 2 – pull mode
6.05330.110	IC Equipment: Inline Ultrafiltration 2 – push mode

### **Chromate in soil and air samples**

2.940.1100	940 Professional IC Vario ONE
2.943.0110	943 Professional Reactor Vario
2.944.0010	944 Professional UV/VIS Detector Vario
2.858.0020	858 Professional Sample Processor – Pump
2.800.0010	800 Dosino
6.3032.150	Dosing Unit 5 mL
6.2041.440	Sample Rack 148 x 11 mL
6.1006.530	Metrosep A Supp 5 - 250/4.0
6.1006.500	Metrosep A Supp 4/5 Guard/4.0
6.6059.312	MagIC Net 3.1 Professional
6.1020.030	Metrosep A Supp 10 - 250/4.0
6.1020.500	Metrosep A Supp 10 Guard/4.0

### **Anions and cations in soil samples**

2.940.2500	940 Professional IC Vario TWO/SeS/PP
2.850.9010	IC Conductivity Detector (2 x)
2.858.0020	858 Professional Sample Processor – Pump
2.941.0010	941 Eluent Production Module



6.2041.440	Sample Rack 148 × 11 mL
6.1006.530	Metrosep A Supp 5 - 250/4.0
6.1006.500	Metrosep A Supp 4/5 Guard/4.0
6.1050.430	Metrosep C 4 - 250/4.0
6.1050.500	Metrosep C 4 Guard/4.0
6.2842.000	MSM-HC Rotor A
6.6059.312	MagIC Net 3.1 Professional

#### Saccharidic tracers in aerosols by IC

2.930.2160	930 Compact IC Flex Oven/Deg
2.850.9110	IC Amperometric Detector
2.858.0020	858 Professional Sample Processor – Pump
6.2041.440	Sample Rack 148 × 11 mL
6.5337.010	IC Equipment Wall-Jet cell for Carbohydrate Analysis
6.1090.420	Metrosep Carb 2 - 150/4.0
6.1090.500	Metrosep Carb 2 Guard/4.0
6.6059.311	MagIC Net 3.1 Compact

#### Anions and cations in aerosols (PILS-IC)

2.940.2500	940 Professional IC Vario TWO/SeS/PP
2.850.9010	IC Conductivity Detector (2 ×)
2.136.0400	PILS, Particle into Liquid Sampler
2.136.0500	Peristaltic Pump, 8 channels with 6 rollers
6.5335.000	IC Equipment for Liquid Handling Set for PILS
6.1825.290	PEEK sample loop 250 µL
6.1006.510	Metrosep A Supp 5 - 100/4.0
6.1006.500	Metrosep A Supp 4/5 Guard/4.0
6.1050.410	Metrosep C 4 - 100/4.0
6.1050.500	Metrosep C 4 Guard/4.0
6.2842.000	MSM-HC Rotor A
6.6059.312	MagIC Net 3.1 Professional



#### Further application-specific equipment

For sample delivery, it is possible to use a vacuum pump with a drying system made by KNF (vacuum pump N840.3ft.40p). The gas phase is separated with denuder systems (e.g., Multi Channel Annular Denuders made by URG, model no. URG-2000-30x242-4CSS). Intake systems such as the cyclones made by URG (e.g., PM 2.5 URG, model no. URG-2000-30EH) allow aerosols to be differentiated by particle size.

#### Voltammetry

2.884.0110	884 Professional VA manual for Multi-Mode Electrode (MME)
2.884.1110	884 Professional VA semiautomated for 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 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-Elektrodenkit with Multi-Mode Electrode
6.6065.202	viva 2.0 Full





### VoltIC Vario pro

VoltIC Vario pro I Heavy metals are determined by voltammetric measuring stand, anions and cations by ion chromatography.

### TitriC Vario pro

TitriC Vario pro I The basic system: pH value, conductivity, and temperature are determined by direct measurement, anion concentrations by ion chromatography, and m value as well as p value plus Ca and Mg by titration.

TitriC Vario pro II The advanced system: pH value, conductivity, and temperature are determined by direct measurement, anion and cation concentrations by ion chromatography, and m and p value by titration.

TitriC Vario pro III The high-end system: pH value, conductivity, and temperature are determined by direct measurement, anion and cation concentrations by ion chromatography, and m and p value by titration. Additionally, this system is equipped with a Discover function for the automatic removal of the sample caps.

### 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
MARGA	Online Analyzer for continuous monitoring of aerosols and gases in ambient air
7010 TOC	Analyzer for determination of the total organic carbon content (TOC) in liquid samples
Furthermore, we offer the Plug and Analyze Series – ICON Analyzer and Alert Ion Analyzer for single method, single component water analysis.	

Please contact your Metrohm supplier for further information. Please also consult [www.metrohm.com](http://www.metrohm.com)





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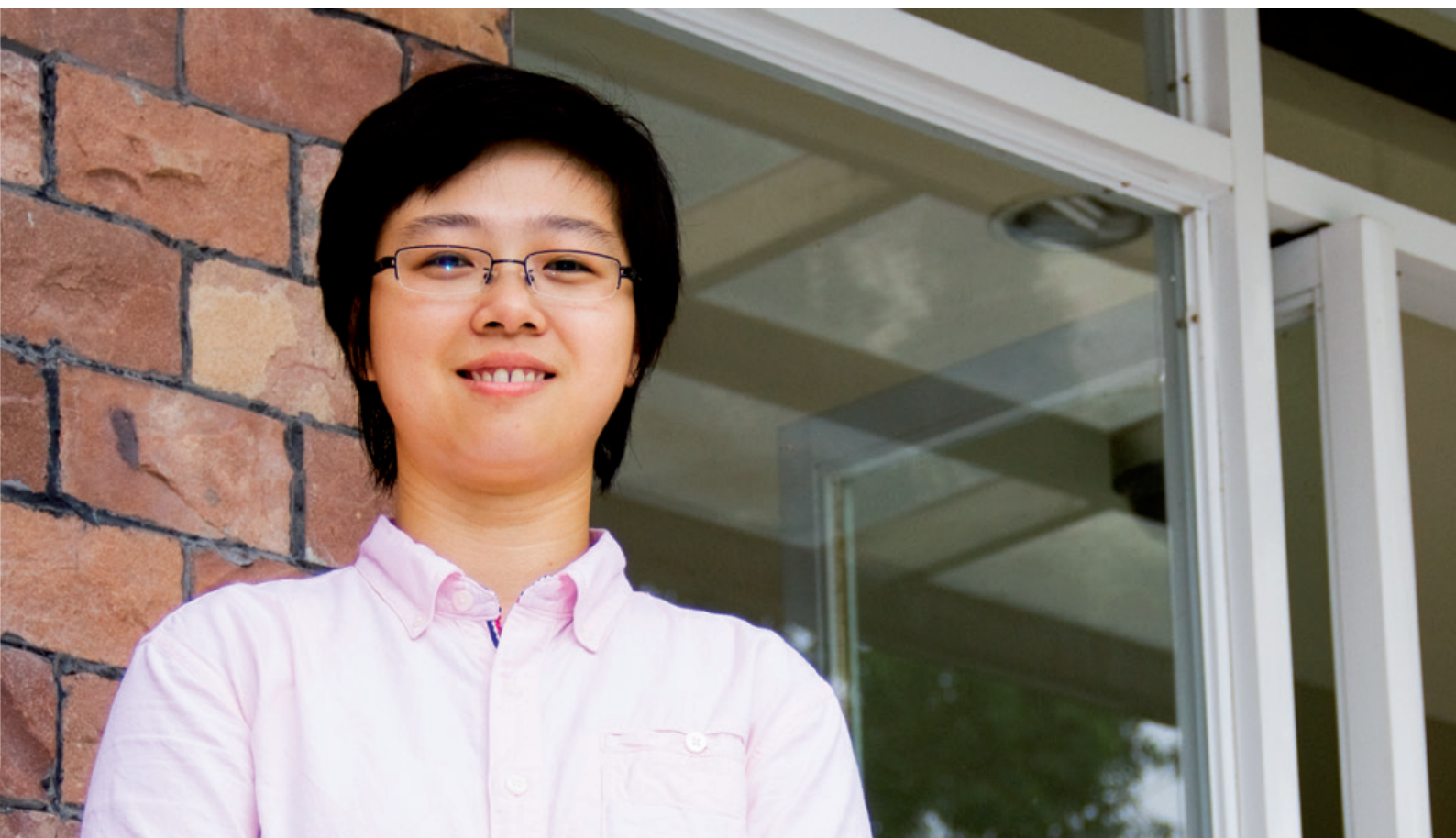
 **Metrohm**

## State-of-the-art environmental analysis in China

The Institute of Tropical and Marine Meteorology is located in Guangzhou in Southern China. One of the institute's missions is to extend the monitoring station's observation capabilities to aerosols and gases to study their influence on the climate and air quality in the Pearl River Delta. To this end, they have acquired a MARGA system from Metrohm Process Analytics.

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Fei Li, researcher at the Institute of Tropical and Marine Meteorology, Guangzhou, China



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